THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

STUDIES OF HIGH POLYMER DEGRADATION

By

THERMAL VOLATILISATION ANALYSIS.

by

DONALD NEIL B.Sc. (Glasgow), A.R.I.C.

SUPERVISOR:

DR. I.C. McNEILL.

CHEMISTRY DEPARTMENT,

UNIVERSITY OF GLASGOW.

SEPTEMBER, 1968.

P R E F A C E.

The work described in this thesis was carried out during the period October 1965 to September 1968 at the University of Glasgow, in the Department of Physical Chemistry, which is under the supervision of Professor J.M. Robertson, C.B.E., F.R.S.

I am indebted to the Science Research Council for the award of a Research Studentship, during the tenure of which this work was carried out.

My thanks are also due to my colleagues in the Macromolecular Chemistry Group for invaluable assistance and discussion, and to various members of the technical staff of the Chemistry Department, in particular Messrs. G. Perrit and G. McCulloch, who carried out the molecular weight determinations.

Finally, I would like to thank my supervisor, Dr. I.C. McNeill, for suggesting the topic of this thesis, and for his general supervision and constant encouragement throughout the work.

C O N T E N T S.

CHAPTER THREE. Page.

CHAPTER ONE.

A. POLYMER DEGRADATION MECHANISMS.

In the broadest sense the term "degradation", when applied in polymer chemistry, can imply any process leading to a chemical change of the polymer structure. It has been found that polymer molecules can undergo chemical transformation under the action of various agencies, both physical and chemical, notably heat, radiation, mechanical stress or shock, and oxygen. Industrially, attention is focussed on those processes which produce deterioration in the useful physical characteristics of the material. In the course of processing, or in subsequent use, a polymer may be subjected simultaneously to a combination of degradative forces. However, most systematic studies of polymer degradation have been limited to the less complicated situation of examining the influence of a single agency, under carefully controlled conditions, on the polymer structure.

In this chapter discussion will be limited to the chemical effect of heat on vinyl polymers with the general structure $-(CH_2—CXY)_n-$ where X and Y can be H or a functional group, since only polymers of this type will be encountered in subsequent chapters.

CLASSIFICATION OF REACTION TYPES.

It has been recognised that thermal degradation reactions in polymers may be broadly classified into two groups:- Chain Scission Reactions and Substituent Reactions. (1)

Chain scission reactions are accompanied by breakdown of the polymer chain, leading to the production of chain fragments, ranging down in size to monomer. The residue may retain the chemical characteristics of the parent material, in that monomer units are recognisable in it.

Substituent reactions are characterised by the elimination or modification of pendant groups, X and Y. The resulting residue progressively changes in character from the original starting material, as the reaction goes to completion. In effect, a new polymer structure arises, and any volatile products are unlike monomer.

Both types of reaction will be encountered in later chapters. It is therefore appropriate to discuss each class in more detail.

CHAIN SCISSION REACTIONS.

Two limiting types of chain scission reactions have been recognised. The first is exemplified by polymethylene which, on pyrolysis, yields a wide spectrum of hydrocarbons from C_1 to C_{70}. (2) It has been established that the degradation of this polymer involves random scission of carbon-carbon bonds, producing polymer radicals, which then undergo mutual disproportionation,

or hydrogen abstraction reactions. This process continues until the molecules so produced are of sufficiently low molecular weight to be volatile at the temperature in question. The random nature of the reaction is borne out by the existence of a rate maximum at 25% conversion, which is predicted by random theory. (2)

The second type of chain scission process, found in poly(methyl methacrylate), is that leading to high yields of monomer as the main volatile product. This proces is visualised as involving an initial homolytic scission, producing polymer radicals, which then split off monomer units, by an "unzipping" process, analogous to a reverse polymerisation reaction. (3)

In practice, few polymers degrade by these limiting processes, but tend to give monomer yields less than 100% yet greater than would be predicted by random scission alone.

A common reaction scheme can be written for all types of chain scission processes, which incorporates the essential features of the reaction, namely Initiation, Depropagation, Transfer and Termination:-

Random Initiation

$$M_n \longrightarrow P_j + P_{n-j}$$

Terminal Initiation

$$M_n \longrightarrow P_1 + P_{n-1}$$

Depropagation

$$P_i \longrightarrow P_{i-1} + M_1$$

Transfer

$$P_i + M_n \longrightarrow M_i + P_n$$

$$P_n \longrightarrow P_j + M_{n-j}$$

Termination by Disproportionation

$$P_i + P_j \longrightarrow M_i + M_j$$

Termination by Combination

$$P_i + P_j \longrightarrow M_{i+j}$$

(Where M_x and P_x represent polymer molecules, and polymer radicals respectively, x monomer units in length).

Thus we can qualitatively explain the degradation of polymethylene as involving random initiation, followed by transfer, or termination by disproportionation. The low monomer yield (.03%) is evidence that depropagation plays little part in the reaction scheme.

In poly (methyl methacrylate), two modes of initiation are believed to occur [1,5]. Radicals can be produced at chain ends in polymers possessing unsaturated end structures. At higher temperatures, main chain carbon-carbon bonds can break, again producing radicals. In either case of initiation, the radicals so formed depropagate almost quantitatively, to monomer.

In the study of chain scission processes, four aspects of the decomposition reaction, listed below, should be examined, with a view to determining the relative importance of the possible radical reactions in any particular polymer:-

(a) The nature and relative proportions of the volatile products.

(b) The relationship between the initial molecular weight of the starting material and the decomposition behaviour of the polymer.

(c) The manner in which the molecular weight of the residue changes as a function of conversion during the course of pyrolysis.

(d) The kinetic features of the reaction.

The product ratio of monomer: total volatiles reveals the relative importance of depropagation and transfer reactions in the degrading polymer. It should be borne in mind, however, that the distribution of products may be markedly affected by changing the experimental conditions employed.

In the case of reactions initiated at chain ends, the initial rate of decomposition will be inversely proportional to the molecular weight. In general, study should be made of the effect of conditions of polymerisation, nature of initiator system employed, etc. on the subsequent thermal stability of the polymer.

Chain ends in poly (methyl methacrylate) samples which have been prepared using free radical catalysts are known to be points of initiation for the depolymerisation. By contrast, anionically prepared polymer does not possess labile chain ends.[5,6]

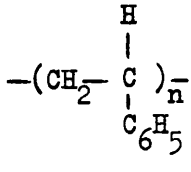
Chain scission processes in which monomer yields are low are usually associated with a rapid fall in molecular weight of the residue. Each act of scission contributes to an increase in the number of molecules. Depropagation, which leads to the ultimate disappearance of molecules rapidly after the initial scission, is more generally accompanied by gradual changes in molecular weight. [7]

A kinetic analysis of the various processes occurring in a degrading polymer, as an integral part of the studies discussed above, may be of great assistance in determining the point of initiation, kinetic chain length, and mode of termination of the radical reactions. Many mathematical models of depolymerisation reactions have been devised in recent years, which have considerably improved our understanding of the basic processes involved. Care must be taken, however, to ensure that the assumptions made in such treatments are reasonable approximations to the actual experimental conditions.

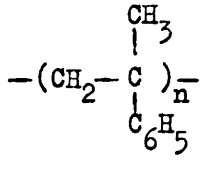
A clear relationship has been found to exist between the chemical structure of a polymer and the proportion of monomer in the degradation products.

Increasing substitution in the polymer chain reduces the potential number of transfer sites, by shielding the chain sterically from radical attack. While it is believed that tertiary hydrogen atoms would be more susceptible to transfer reactions than secondary or primary [8], the availability, rather than reactivity of hydrogen atoms, appears to be the dominant consideration.

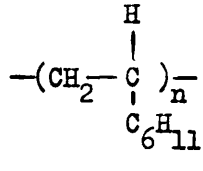
Highly substituted radicals are believed to be more stable electronically [9], and thus less likely to attack C-H bonds. Increasing substitution of the radical would also be expected to prevent sterically the close approach between radical and polymer molecule required for intermolecular transfer. For these reasons, tertiary radicals are believed to be least active in transfer reactions, while primary radicals are the most active. The effect on the monomer yield is illustrated in the case of styrene polymers (a) to (c) :-



(a)



(b)



(c)

The monomer yield from polystyrene (a) is 40% at 300-400°C, [10] while in poly (alpha methyl styrene) (b), it is 100% [10]. This can

be explained by the additional methyl group inhibiting transfer, by replacing a tertiary hydrogen, and also stabilising the first formed radical electronically by an inductive or hyperconjugative effect. The monomer yield from hydrogenated polystyrene (c) is less than 5% [10]. The cyclohexane ring hydrogens are more easily abstracted than the aromatic hydrogens in polystyrene. The first formed radical from (c) would be expected to be less stable electronically than that from (a), since delocalisation of the unpaired electron by the aromatic nucleus is possible in (a), but cannot occur in (c).

SUBSTITUENT REACTIONS.

Substituent reactions, which may compete with or supplant chain scission processes, can be classified into three main types:-

(a) Elimination Reactions.

(b) Ester Decomposition Reactions.

(c) Cyclisation Reactions.

Type (a), illustrated by poly (vinyl chloride), involves the elimination of HCl, producing a conjugated polyene chain:-

$$-CH_2-CHX-CH_2-CHX- \longrightarrow -CH=CH-CH=CH- + HX \quad (X = Cl)$$

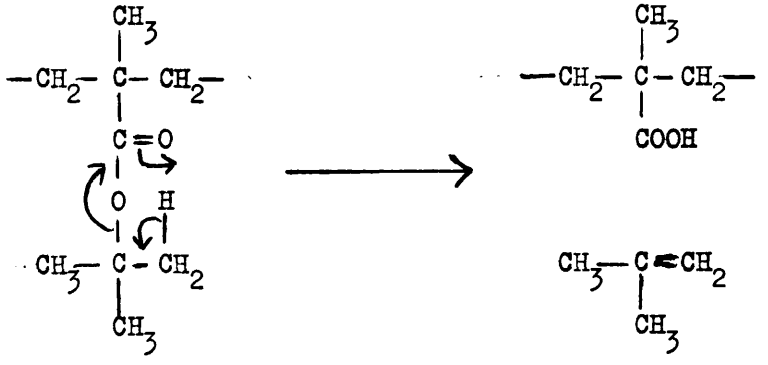
Analogous processes are known where X = OH, Br, $O-\overset{\overset{O}{\|}}{C}-CH_3$

The mechanism of elimination of HCl from poly (vinyl chloride) has not been clearly elucidated. Theories have been

put forward that the process is respectively ionic [11], molecular [12], or radical [13] in nature. Any mechanism must satisfactorily explain the action of the wide number of stabilisers which have successfully been used for this polymer.

The radical mechanism appears to be favoured by most workers, but factors such as the autocatalytic nature of the reaction have not been explained by this hypothesis. This controversy will be discussed in more detail in a later chapter.

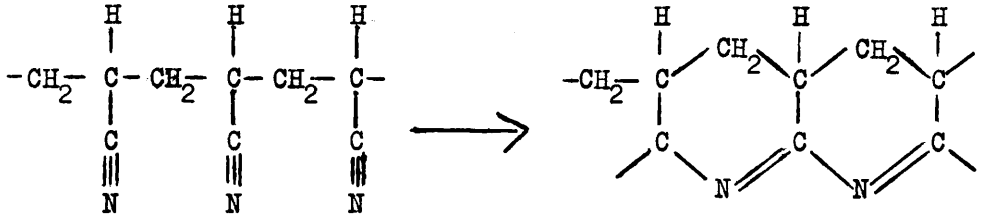
Ester decomposition reactions, involving the production of the parent acid, together with an olefin, have been encountered in polymer decomposition. This process is exemplified by poly (t - butyl methacrylate), which is known to liberate butene, leaving a poly (methacrylic acid) residue as the first formed product [14]:-



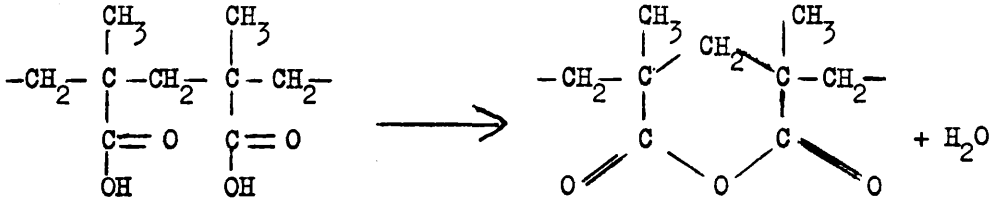
The residue produced, although polymeric, is unlike the parent material.

In type (c) reactions, side groups undergo rearrangement to give cyclic polymeric structures.

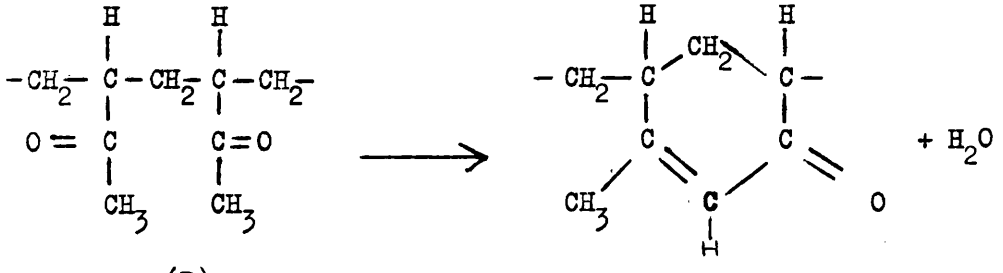
The reaction need not involve the elimination of volatile products, as in poly (acrylonitrile) [15,16] :-



Cyclisation reactions may also proceed with concurrent elimination of small molecules, as in poly (methacrylic acid) [17] (A), and poly (methyl vinyl ketone) [18] (B).



(A)



(B)

The mutual interaction of pendant groups may also occur intermolecularly, leading to a cross linked network.

The wide diversity of Substituent reactions does not

permit a common reaction mechanism to be written. However, several features common to substituent reactions emerge:-

(a) They lead to the formation of products structurally dissimilar to the original polymer.

(b) The final product, (at temperature in excess of 500°C) is usually a carbonaceous residue, often akin to graphite [19]. This is due to the initial formation of cyclic or cross linked structures which, rather than volatilising completely, may undergo reorientation, and dehydrogenation, to give an almost pure carbon.

(c) Substituent reactions frequently lead to coloration of the residue, due to the formation of conjugated unsaturated structures. In the case of PVC, for example, the chromophore is believed to be a polyene which may possess at least 20 double bonds in conjugation [20].

(d) Substituent reactions often commence at temperatures below those at which depolymerisation occurs. The Substituent reaction, if allowed to proceed to sufficient extent, will also inhibit any potential depolymerisation processes. This is due to the formation of structures which do not permit depropagation processes to pass through them. An example of such behaviour is polymethacrylonitrile, where cyclisation occurs at lower temperatures than monomer production [21].

GENERAL CONSIDERATIONS.

The ultimate aim of studies of degradation is the prediction of the thermal stability of a polymer, given its chemical constitution. Ideally, we would seek to be capable of forecasting the temperature at which breakdown will commence, and the major products of the reaction.

Such detailed predictions are not yet feasible, although some generalisations can be made concerning the relationship between structure and thermal stability:-

(a) Degradation processes are often initiated at weak structures or structural abnormalities present in extremely small concentrations in the polymer backbone. The chain end initiated depolymerisation of poly (methyl methacrylate) has already been mentioned. The dehydrochlorination of PVC is also believed to be initiated at chain ends, although peroxide structures may also be responsible [22]. Small traces of copolymerised acid impurity greatly reduce the thermal stability of polymethacrylonitrile [23]. The conditions of polymerisation and the history of the monomer used to prepare the polymer may therefore have a profound influence upon its subsequent thermal stability.

(b) In polymers, many processes which can occur in small molecules are converted to chain reactions by the polymer

environment. As a result, the study of the behaviour of "model" compounds of low molecular weight cannot be expected to elucidate completely the mechanism of degradation of macromolecular analogues.

(c) The mechanism of degradation of copolymers cannot necessarily be deduced by extrapolation from the processes occurring in the parent homopolymers. For example, copolymers of methyl methacrylate and vinylidene chloride are less stable than either homopolymer, yielding methyl chloride as a major volatile product, rather than the expected methyl methacrylate and hydrogen chloride [24].

(d) The formation of discrete ions in decomposing organic polymers is unlikely, since the charge cannot be delocalised by solvation, and the dielectric constant of molten polymer is generally too low to support charge separation. Most polymer degradation mechanisms, in bulk, are therefore believed to involve uncharged intermediates, occurring via "radical" or "molecular" pathways. Ionic or "ion pair" intermediates may be possible in solution degradation however, or in highly polar polymers.

B. METHODS OF STUDYING THERMAL DEGRADATION.

OBJECTIVES OF STUDY.

Any thorough investigation of polymer degradation should

seek to obtain the following information:-

(a) The nature, quantity, and rate of formation of the volatile products of reaction.

(b) The identity of any new structures which might appear in the residue, and the rate of any such structural change.

(c) The changes in molecular weight of the residue, measured as a function of time or extent of reaction.

(d) The chemical kinetics (kinetic parameters) of the process.

The accumulation of most or all of this information is necessary before the mechanism of the process can be clearly established.

POSSIBLE SOURCES OF ERROR.

Studies of polymer degradation are complicated by the attention which must be paid to the experimental conditions employed. It has been recognised that several factors must be taken into consideration in this context. Since each of these is a potential source of systematic error, it is appropriate to discuss them at this point.

(a) Sample Form and Size.

Although degradation studies can be conducted in solution, the more general method of study is to pyrolyse a solid sample of the polymer. A molten polymer is rarely a free flowing liquid, and some polymers commence decomposition before fusion. The ease with

which the volatile products of the reaction may diffuse through the polymer mass is largely determined by the viscosity of the heated sample. Care must therefore be taken to ensure that the film thickness, or particle size employed, is not such as to cause a diffusion controlled process to occur. Initially formed products, arising at the base of the sample, may take a significant time to reach the exterior of a viscous or thick sample. These entrained products may be cracked further in the hot zone, may recombine, or may catalyse the decomposition process. Each of these factors gives rise to erroneous rate measurements.

Owing to poor heat transfer, thick samples may suffer from temperature gradients, causing different rates of decomposition to operate at different locations in the sample. For any fundamental study therefore, the sample should be finely divided, as a thin layer or film, and prepared reproducibly for degradation. Tests should be performed, where possible, to ensure the absence of diffusion control.

Examples of diffusion controlled processes are well authenticated. For instance, Barlow, Lehrle and Robb [25] showed that above a limiting thickness, monomer production from poly (methyl methacrylate), and polystyrene was diffusion controlled, and Vassallo [26] demonstrated that thin films of polypropylene degraded more rapidly than thicker films of the same

weight. Smith, [27] however, showed that the decomposition of some amorphous polymers was not diffusion controlled. It has been demonstrated by Jones and Moyles that in the degradation of polystyrene, the yield of monomer as a percentage of total volatiles increased when extremely small samples were degraded, by comparison with larger samples, [28] suggesting that not only the rates of formation of the products, but the nature of the products themselves, may be a function of sample form.

(b) External Atmosphere.

The rate at which the volatile products of degradation leave the sample can be affected considerably by the external pressure above the polymer. Again, secondary reactions may take place, either within the sample itself, or in the hot zone above the sample, if molecular collisions are permitted. In general the reaction tends to be more complex, the greater the external pressure.

An example of this behaviour is the pyrolysis of poly (tetrafluoroethylene), where the product ratio of monomer: total volatiles falls as a function of increasing external pressure. [29] While monomer is believed to be the first formed product at all pressures, it is highly reactive, and recombines in the hot zone at elevated pressures. It has also been shown by Madorsky [30] that in the pyrolysis of

polymethylene, conducted both in vacuum and in a helium atmosphere, the product distribution of the liquid fraction was markedly different in the two cases.

Phenomena of this kind have led to the use of high vacuum systems, or alternatively a dynamic inert atmosphere, for the study of polymer degradation, so that the products are removed from the sample area as rapidly as possible after formation. It is also important to exclude oxygen from any experiment, owing to its considerable reactivity.

(c) Heat Input.

The temperature, in an isothermal experiment, or the rate of heating in a temperature programmed study, not only alters the rate of reaction because of the exponential relationship between rate and temperature, but can also affect the composition of the products formed during pyrolysis. This may be related to several factors which are temperature dependent:-

(i) At elevated temperatures the degrading polymer may be less viscous, permitting initially formed products to escape more readily.

(ii) The degradation products may undergo secondary reactions more readily at higher temperatures.

(iii) Polymer radicals may react by a variety of processes, according to their temperature of formation.

Polystyrene and poly (methyl methacrylate), at temperatures in excess of 800°C yield an increasing proportion of products which are of lower molecular weight than monomer.[31,32] This is presumably attributable to decomposition of initially formed monomer at high temperatures.

In poly methacrylonitrile, however, it has been established that monomer yields increase, at the expense of side chain cyclisation processes, as a function of increased temperature in an isothermal experiment or of faster heating rates in temperature programmed studies.[21,33]

Factors of this kind must be borne in mind when comparing results obtained under widely differing thermal conditions.

(d) Geometry and Material of Sample Holder.

Studies have shown, particularly in the field of thermogravimetry that the behaviour of a sample on heating may be a function of the geometry of the sample container. While this may be related to buoyancy effects in thermobalances,[34] poorly designed sample holders may impede volatilisation, or introduce heat transfer problems.

More serious, however, is the possibility of catalytic

effects being exerted by some container materials on the breakdown of polymers, or the reaction of the products themselves with the sample vessel. An example of the latter behaviour is the reaction of silica vessels with the products of decomposition of fluorocarbon polymers [35].

All of the above factors must be considered in designing, and interpreting the results of experiments which investigate polymer degradation.

TRADITIONAL METHODS OF STUDY.

Many systems have been devised for the study of polymer degradation. The approach adopted is largely determined by the objectives of the study, and the polymer system in question. Normally however, a degradation apparatus will incorporate facilities for isolation of products for subsequent analysis, and for measurement of rates of decomposition. Adequate temperature control is also essential.

Product analysis can be a major problem in polymer degradation studies. This is due to the complex mixtures of products, often isomeric, or with similar functional groups, which are evolved during pyrolysis. Gas-liquid chromatography, mass spectrometry and infra red spectroscopy have been successfully applied in most cases, however. It is

particularly important that the analytical process be applied as soon as possible after product collection, to minimise errors due to recombination or decomposition of the first formed products. Product collection is greatly facilitated when the degradation is performed in vacuo. As previously stated, systems operating under vacuum conditions are also less subject to complications due to slow diffusion of products through the sample, and secondary reactions in the hot zone.

Two general approaches to the measurement of rates have been applied. In the first instance, the weight of the sample is measured at intervals, or continuously, during degradation. The rate of the reaction is therefore obtained in terms of the rate of disappearance of the sample weight in unit time. Various designs of balance for this purpose have been described.[36]

An alternative approach is the measurement of the rate of formation of the volatile products of the reaction, usually by measuring the pressure exerted by the heated sample. Pressure measuring devices used in this context include manometers, Pirani gauge, or spoon gauge. The type of device used in any particular study depends upon the nature of the products, whether or not an intermittent or continuous measurement is desired, and whether the system is hermetically sealed,

or under continuous pumping.

The classical approach to degradation studies is to measure some parameter of the system as the sample is heated under carefully controlled isothermal conditions. The weight changes of the sample, or pressure within the system, or other suitable measurement, is then used to follow the progress of the decomposition.

Isothermal work remains an integral part of any study, but suffers from some disadvantages:-

(a) An investigation over a wide temperature range is tedious and time consuming, and may not reveal all of the processes occurring. (37)

(b) The sample may take a significant time to acquire the isothermal condition. During this "warm up" period some sample decomposition inevitably occurs. Since the system is not in "equilibrium" it is difficult to determine the kinetic features of this stage of reaction. This is a major shortcoming of isothermal work, since study of the initial stages of degradation may reveal the point of initiation of the reaction.

Recent workers have consequently made increasing use of methods whereby the sample is studied under carefully controlled, but non isothermal conditions, the usual approach being to raise

the temperature of the sample linearly. A suitable parameter of sample or system is then measured as a function of the temperature.

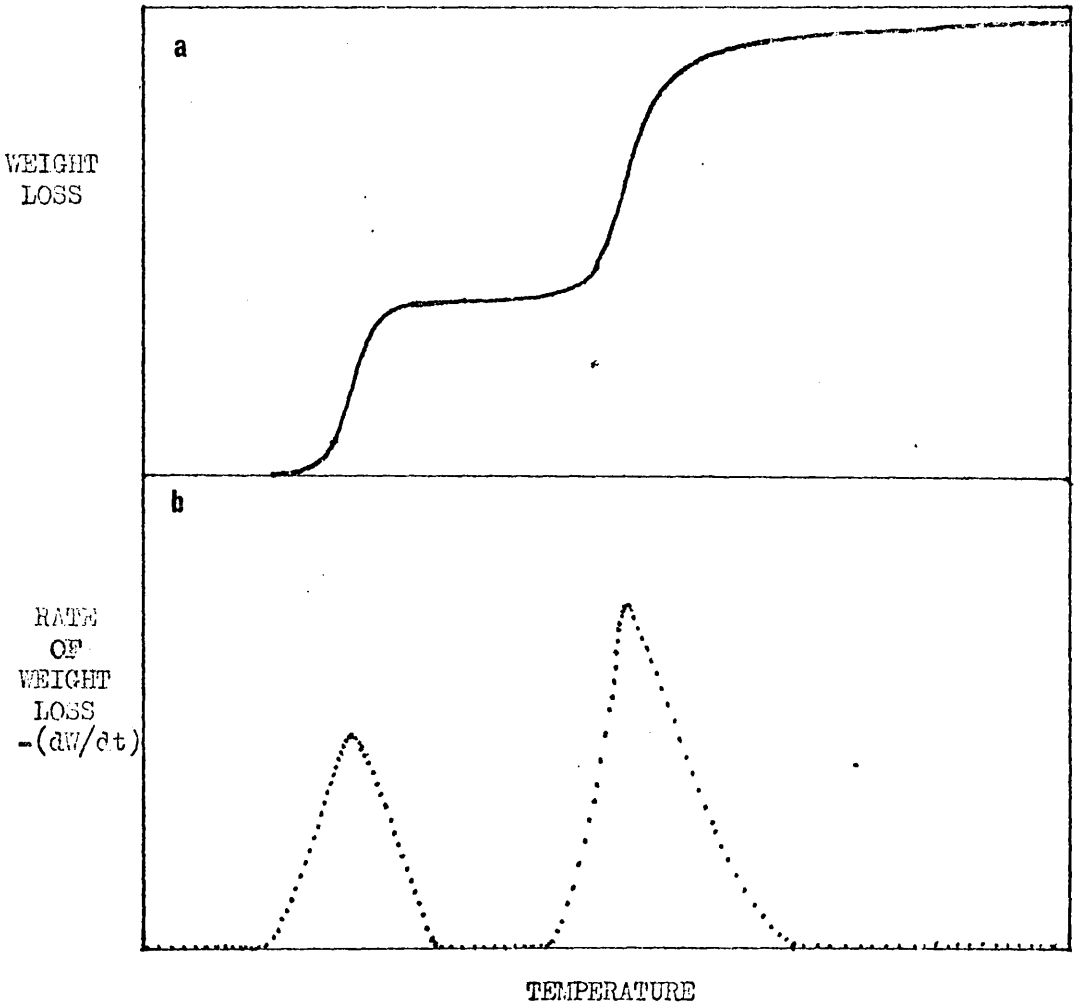
It is a basic assumption of such an approach that if a rate measurement is taken at a temperature T in a nonisothermal experiment, the sample under study will be found to be decomposing at the same rate as it would have been had it attained the same extent of conversion in an isothermal experiment, conducted at the same temperature, T.

Since the substance of this thesis concerns the application of such a technique, it is appropriate to discuss some of these thermoanalytical methods, and their usefulness in studies of polymer degradation, at this point.

NON ISOTHERMAL METHODS OF STUDY.

Thermogravimetry (TG)

Thermogravimetry is possibly now the technique most widely applied in the study of polymer degradation. A sample is continuously weighed, and the weight recorded, as it is heated at a linear rate of temperature rise. The graph of sample weight versus sample temperature, called a thermogram, serves as a record of the decomposition of the material. An example of such a thermogram is shown in figure (1,1).



FIGURE(1,1), Weight loss, and differential weight loss curves for a two stage decomposition.

The technique is obviously useful as a means of rapidly evaluating thermal stability. In the case of polymeric materials, it cannot give information concerning the nature of the volatile products, although in the case of inorganic materials, where the decomposition may be stoichiometric, TG is used as a method of analysis.

The great accuracy of many thermobalances permits the accurate measurement of the overall rate of sample decomposition. In particular, initial rate measurements can be obtained under carefully controlled conditions.

Many treatments have been devised to obtain kinetic parameters from TG, summarised by Flynn and Wall. [38] The major disadvantage of these methods lies in the fact that in many polymer systems, several processes, running concurrently, may lead to weight loss. Kinetic parameters obtained in such cases will be overall decomposition parameters, and may have little mechanistic significance.

The interpretation of TG thermograms is greatly facilitated when a differential or DTG plot is obtained (see figure (1,1)). The rate of weight loss is then plotted as a function of temperature, and minor changes in thermal behaviour rendered observable. Several methods of obtaining

a derivative thermogram have been described. [39]

Thermogravimetry suffers from considerable experimental difficulties, which have been summarised by Wendlandt [40] and by Doyle [41]. The most serious of these can be listed:-

(i) Systematic errors may arise in measuring the weight of the sample. Changing convection currents in the oven may lead to an apparent gain in weight of the sample, owing to changes in "buoyancy". This effect is a function of the geometry of the sample holder, furnace size and shape, furnace temperature, and heating rate. Blank runs must therefore be made to determine the correct base line for the experimental conditions employed.

Badly designed sample holders may also permit the degrading polymer to lose weight by "sputtering", rather than decomposition.

(ii) Decomposing polymers often yield products which are volatile at the temperature of degradation, but involatile at ambient temperatures. Such products may recondense on the balance support mechanism or the sample container itself, leading to erroneous weight loss data.

(iii) A sample holder designed to minimise effects such as (i) and (ii) may be poorly designed for polymer degradation studies. It may necessitate the use of thick or poorly subdivided samples,

and may preclude the reproducible casting of polymer films on the degradation crucible. Small sample holders (i.e. of low thermal capacity) may suffer a temporary difference in temperature from that registered by the measuring thermocouple, when endothermic or exothermic processes are occurring in the sample. This problem is accentuated when the thermocouple probe is remote from the sample container, as is often the case.

In general, therefore, commercial TG instruments may require considerable modification before they are satisfactory for the study of polymer degradation.

Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC).

In both DTA, and DSC, the heat effects associated with physical or chemical changes are recorded as a function of linearly increasing temperature.

In DTA, the temperature differential between the sample under study, and a reference material, is recorded as a function of temperature. In practice this is achieved by opposing the outputs from a thermocouple in the sample, and a similar thermocouple in the reference material, and measuring the imbalance potential between the two. The sign of this imbalance

signifies the exo- or endothermic nature of the processes occurring, while the magnitude is proportional to the temperature differential.

As in TG, the nature of the products of decomposition is not revealed by DTA. Degradation of the polymer is registered as a peak, the area enclosed by which is proportional to the total heat change occurring in the sample. This thermogram can be used, after suitable calibration, to determine the heat of reaction for the process concerned, giving access to useful thermodynamic information. Several sources of error must be overcome however, before meaningful quantitative information can be obtained:-

(a) Data treatment is complicated in cases where significant volatilisation occurs, since the thermal capacity of the system changes during degradation at a rate proportional to the rate of weight loss of the sample. The loss of products may also cause cooling of the sample to occur, leading to erroneous temperature measurements.

(b) Part of the heat produced in the sample may be lost by conduction along the thermocouple wires, and therefore too low a sample temperature may be registered.

(c) Thermal gradients may exist within the sample, owing to

heat transfer problems. Care must therefore be taken to ensure that the thermocouple bead is inserted reproducibly into the body of the sample, and excessively large samples must be avoided.

(d) The experimental conditions of the degradation often involve intimate packing of the sample, which may cause any volatilisation process to become diffusion controlled.

(e) As in TG, the geometry and material of the sample holders have a considerable influence on the shape of thermogram produced.

Some of the problems associated with DTA are reduced in the sister technique of Differential Scanning Calorimetry. (42) In this method, the sample temperature is held isothermal to a reference substance (or furnace block) by supplying heat to the sample or reference. The amount of heat required to maintain isothermal conditions is recorded as a function of linearly increasing temperature. Polymer decomposition is thus detected in terms of an enthalpy curve. Since heat changes are recorded directly, heats of reaction can be obtained without the calibration procedure necessary in DTA. Many of the sampling difficulties in the latter can also be eliminated. The technique is probably therefore a more powerful quantitative tool than DTA,

and all of the information obtainable by DTA can be obtained by DSC.

Torsion Braid Analysis (TBA).

Polymer decomposition has been studied by Gillam and Lewis [43] by the indirect method of Torsion Braid Analysis. The polymer under study is coated onto a pendulum which consists of a loose braid of glass fibres. The mechanical properties of the composite are investigated by observation of the torsional oscillations of an inertial mass, which is suspended by the shaft, and periodically set into vibration.

Changes in polymer structure, related to molecular weight changes, degree of crosslinking etc., cause changes in dynamic mechanical behaviour, and hence in the period of the oscillation of the pendulum. This technique has been applied isothermally, and at a non linear rate of temperature rise.

Electro Thermal Analysis.

The continuous measurement of electrical conductivity of a sample as a function of increasing temperature has been termed Electro Thermal Analysis by Pope [44]. Changes in electrical conductivity may accompany the formation of new structures in the sample, which would appear to make the technique potentially useful in the study of Substituent Reactions of polymers. The

technique has been applied to the study of PVC degradation [44] and the pyrolysis of phosphonitrilics [45], but is not yet widely used.

Gas Effluent Analysis (GEA). [45]

Polymer degradation is normally accompanied by the evolution of volatile material, the identification of which is a prerequisite of any complete study of the process. The techniques so far discussed are only useful in giving information about structural changes in the remaining residue. The realisation of this limitation has resulted in the development of a number of techniques designed to give information concerning the nature, and rate of formation of the products of the decomposition.

The simplest gas effluent analysis technique involves the detection of the pyrolysis products by a thermal conductivity detector. In this way, the product evolution can be monitored as a function of temperature. Most of the techniques described involve purging the heated sample with a steady rate of flow of inert gas, which carries the effluent gases past the detector as they are produced. Under these circumstances, the response of the detector is a function of the rate of the degradation reaction. The GEA peak should

thus be directly related to a DTG peak, or a DTA peak associated with decomposition.

This equivalence has been confirmed by authors employing combined GEA/TG, or GEA/DTA [46]. Combined DSC/gas evolution is incorporated in commercially available instruments. [42]

Unless a single product is formed during the reaction (which is not generally the case), the information given by these techniques will be difficult to translate into quantitative terms. This is because the detectors so far developed have a different response to each of the various components of the mixture.

Vassallo [26], and Rogers [47], have made some attempt to overcome this difficulty. Employing a thermal conductivity cell as the detector, they interposed between this and the pyrolysis crucible a combustion chamber consisting of cupric oxide heated to 800°C. Any organic compounds in the volatile material were thus converted to carbon dioxide and water.

An alternative approach to mixed gas evolution is the selective absorption or condensation by chemical or physical means, of some of the components of the gas stream [48]. This procedure is more suitable for following the decomposition of inorganic materials, rather than organic polymers, however,

since the products from the latter are rarely sufficiently different in chemical constitution to permit separation in this way.

Torsion Effusion Analysis.

The measurement of rate of volatilisation of a poly (tetrafluoroethylene) sample has been described by Rosen and Melveger by a Torsion Effusion technique [49]. Rather than employing a gas detector as the sensor, the gaseous molecules escaping from the heated sample are permitted to flow through eccentrically placed orifices in the sample crucible. The crucible is suspended from a tungsten torsion wire, which experiences an angular displacement due to the force created by the escape of the volatiles. It can be shown that the force produced by the effusing molecules causes a deflection dependent upon the rate of the reaction, the temperature of the measurement, and the molecular weight of the vapour. In principle, therefore, the issuing gas may be identified, and kinetic parameters calculated for the reaction leading to its formation.

Such a technique has an advantage over conventional methods of GEA in that the molecular weight of the volatile material may be obtainable, and the product identified.

Where mixtures of compounds are produced, the value

obtained would be a composite one, and difficult to interpret. Care must also be taken to ensure that the molecules have reasonably unimpeded passage from the heated sample, to the gas outlets.

Mass Spectrometric Thermal Analysis (MTA or MSA).

Mass spectrometry is now a routine analytical tool in determining the nature of the products of a degradation reaction. In MTA, however, the sample under study is subjected to a linear temperature rise, and the products fed directly, under continuous pumping, (at a vacuum of 10^{-7}mm.) into a rapid scan mass spectrometer. The spectrum of the product stream is then repeatedly scanned as a function of time and temperature.

A typical experimental set up has been described by Friedman (50). In this case a 1mg. sample of polymer was sufficient for a complete study. The effluent gases were pumped through leak containing 821 holes 2 mil in diameter, and allowed to cool to ambient temperature before analysis, since the mass spectrometer sensitivity and fragmentation pattern are temperature dependent.

The identity of any particular product may be revealed by the cracking pattern in the mass spectrometer. The intensity of a peak in the spectrum is proportional to the rate of

formation of the species in question, at the time the spectrum is recorded. Since the sample is under continuous pumping, a plot of peak height versus temperature, will be equivalent to a differential rate plot, and may be of use in determining kinetic parameters for that peak [51].

MTA, especially when applied to the study of complex polymers, yields an enormous quantity of data. Friedman [50] has devised an automatic data collection system, with which it is hoped to obtain computerised qualitative and quantitative analyses.

The major disadvantage of this technique is the considerable expense of the necessary equipment, which makes it impracticable for the average laboratory. It is obviously vastly superior to techniques where the products may have to be stored before analysis.

The small size of sample required does not permit detailed analysis of the residue, and the breakdown pattern of the products may not be completely unambiguous.

Despite these disadvantages, however, the technique is possibly the best single method devised for studying polymer volatilisation.

Flash Pyrolysis.

In the techniques previously discussed, the sample under study is subjected to a gradual increase in temperature, and the decomposition is followed as a function of temperature.

An alternative approach, which has been increasingly applied in recent years, is to subject the material to a pulse of thermal energy, over a short time interval. An example of this approach has been described by Barlow, Lehrle and Robb [52]. The sample, usually less than 2mg, was placed on a filament, situated at the injection port of a gas chromatograph. The filament was then heated by passing a suitable current through the wire for about ten seconds, and the degradation products were swept directly into the chromatograph for immediate analysis. Two ways of heating the sample were described:-

(a) A sufficiently high filament temperature was produced to degrade the sample completely during the heating period.

(b) The sample was only partially degraded, at temperatures lower than (a), so that the residue was available for further degradation pulses, at higher temperatures. In practice, method (b) involved subjecting the polymer to a series of pulses, in steps of 100°C, the products from each pulse being chromatographed before the next pulse was passed.

By either method, the pyrograms obtained were highly characteristic of the polymer in question.

Barlow, Lehrle and Robb [52] took considerable care to determine the operating temperature of the filament, for a particular value of heating current. For temperatures below 800°C, the melting of standard compounds was observed, use being made of an optical pyrometer to measure higher temperatures.

Since gas chromatography has been applied to the identification and quantitative estimation of pyrolysis products, the technique appears to have considerable potential. It has been applied to qualitative examination of polymers, and determination of the degradation kinetics [53].

As in MTA, a major advantage of this technique is the rapidity of the whole operation, and the ability to analyse products immediately upon formation, avoiding side reactions.

In the interests of gas chromatographic resolution, the maximum degradation time is limited to 20 seconds [53]. All the products of degradation are therefore produced rapidly and it may be impossible, particularly when high final temperatures are employed, to tell when the products are liberated, or at what temperature the degradation commences. The "stepped"

pulse technique overcomes this difficulty in some part.

As in MTA, the small sample size employed may preclude analysis of the residue, and considerable care must be taken to obtain unequivocal assignment of the various chromatography peaks. It must also be borne in mind that where samples are heated to temperatures above those used in isothermal studies, in order to obtain a sufficiently large sample for chromatographic analysis, the results may not be strictly comparable to studies carried out under less severe thermal conditions, although no less valuable.

THERMAL VOLATILISATION ANALYSIS, AIM OF THIS WORK.

The large number of techniques described above is an indication of the interest shown in the thermal reactions of polymers. Clearly, no single technique has yet been devised which will completely elucidate the mechanism of a degradation process, without also having recourse to another method of study to supply additional information.

Rather than apply one of the existing methods, McNeill has devised the technique of Thermal Volatilisation Analysis (33,54) (TVA), which, unlike many of the alternative methods, is designed specifically for the study of polymer degradation.

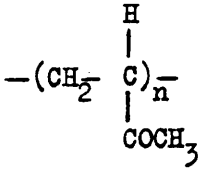
A full description of this method is reserved for

subsequent chapters (II and III). Briefly however, the technique bears closest resemblance to GEA methods. Unlike most of these, however, the sample is continuously evacuated during degradation. A Pirani vacuum gauge is used to record continuously the rate at which volatile material is evolved from the polymer, under conditions of linearly increasing temperature.

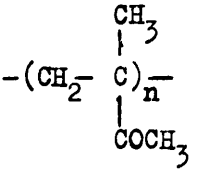
At the commencement of the period of research described in this thesis the potentiality of the technique as a method of studying polymer degradation was largely unknown. It was therefore an objective of this research to assess the technique in this respect. In particular it was clearly necessary to establish the significance of the TVA thermogram.

A further objective of this research was to apply the TVA technique to two specific problems in polymer degradation:-

(i) The comparison of the thermal behaviour of the related polymers poly (methyl vinyl ketone) A, and poly (methyl isopropenyl ketone) B.



A.



B.

(ii) The thermal degradation of polymer blends containing poly (vinyl chloride).

CHAPTER TWO.

THE THERMAL VOLATILISATION APPARATUS.

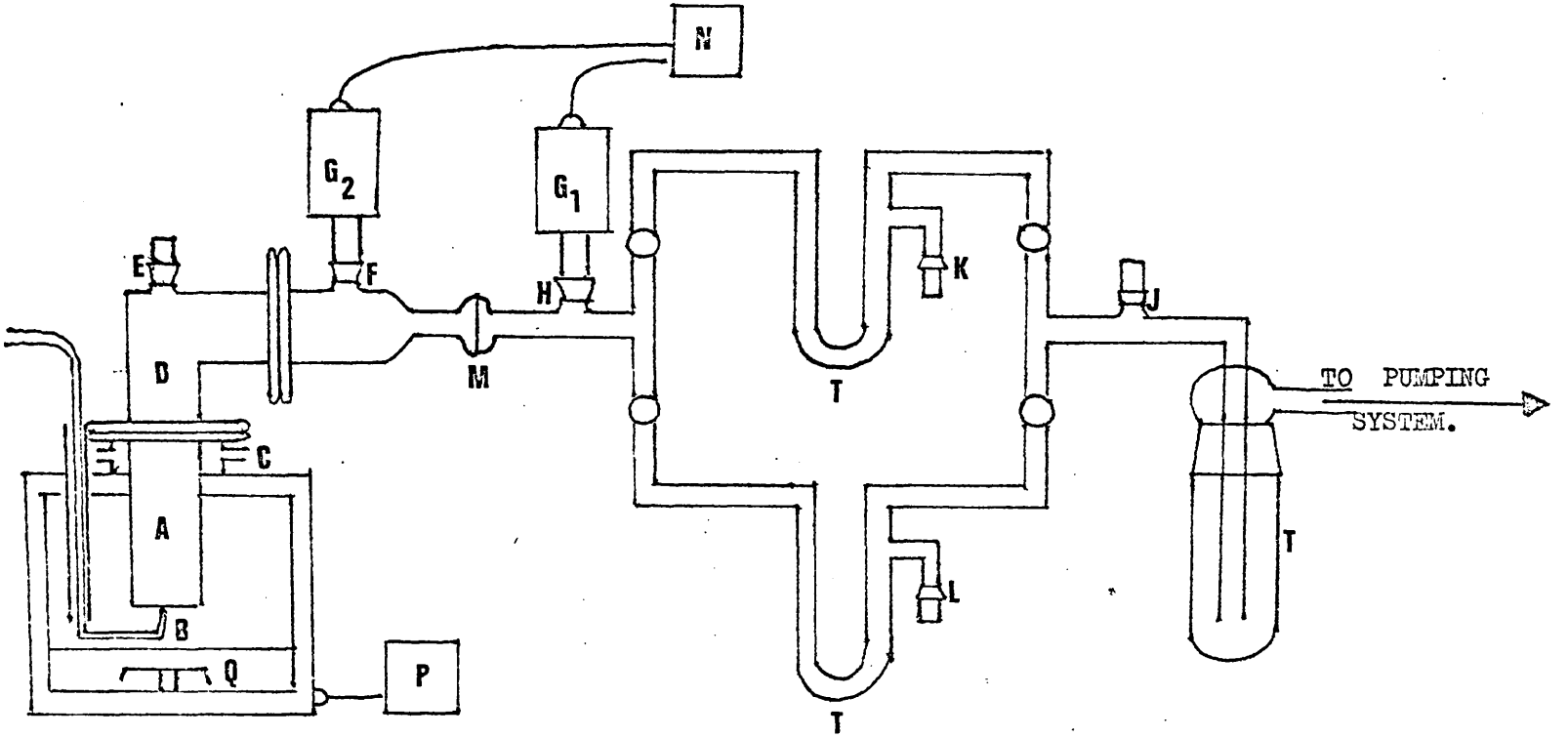
The principal features of TVA are the subject of publication by McNeill [33,54]. For convenience, and owing to the importance of the technique in this work, a full description of the method, and its operation, is given in this chapter.

CONSTRUCTION AND DESIGN OF THE APPARATUS.

A diagram of a TVA apparatus layout is shown in figure (2,1). The vacuum system was constructed of Pyrex medium wall tubing, and was continuously evacuated during an experiment, using liquid nitrogen traps, and vacuum pumps (Edwards model E01 vapour diffusion pump, backed by a model 2SC 20A rotary oil pump).

The degradation tube A, 6 in. in length, was constructed from a Pyrex Quickfit FG 35 flange, and had a flat base. The tube was connected to the vacuum system by means of lid D, which had two FG 35 flanges at right angles, as shown. The upper portion of the tube, and the greased flanged joint, were cooled by the glass water jacket C during the course of an experiment.

As can be seen, two identical, parallel product traps were available. These permitted the isolation of fractions of products, corresponding to a particular temperature range of the



FIGURE(2,1), The TVA Apparatus Layout.

A Degradation Tube.
B Chromel-Alumel Thermocouple Junction.
C Cooling Jacket.
D Removable , Flanged Lid.
E,F,H,J,K, L B.14 Ground Glass Sockets.
G_1, G_2 Pirani Gauge Heads
M Ball And Socket Joint.
N Pirani Control Unit.
P Temperature Programmer.
Q Oven Fan.
T Cold Trap

degradation, without interrupting the experiment unduly.

The oven and linear temperature programmer were Perkin Elmer F 11 instruments, designed for gas chromatography. The oven could operate isothermally, or with temperature programming, for which sixteen switched rates of temperature rise were available, ranging from 1 to 40°C. per minute. The oven had an upper temperature limit of 530°C.

Before use, the oven was fitted with an asbestos lid, with a circular hole, which permitted tube A to be inserted and removed from the top. This hole, and the cooling jacket C, served to locate the tube in the oven reproducibly, before each experiment.

The thermocouple B was constructed of Leeds and Northrup 20 gauge chromel and alumel twin cable, and was held in place in the oven by means of a narrow bore glass tube, the upper portion of which was permanently clamped.

G_1 and G_2 were "Speedivac" Pirani Gauge Heads, model G5C - 2 (Edwards High Vacuum Co. Ltd.,) inserted at B.14 sockets. When connected to the Pirani control unit (Model 8A), the outputs from these heads could be simultaneously recorded during the course of an experiment. The sockets E and J were alternative points of attachment for the gauge heads.

OPERATION OF APPARATUS.

Pirani Gauge.

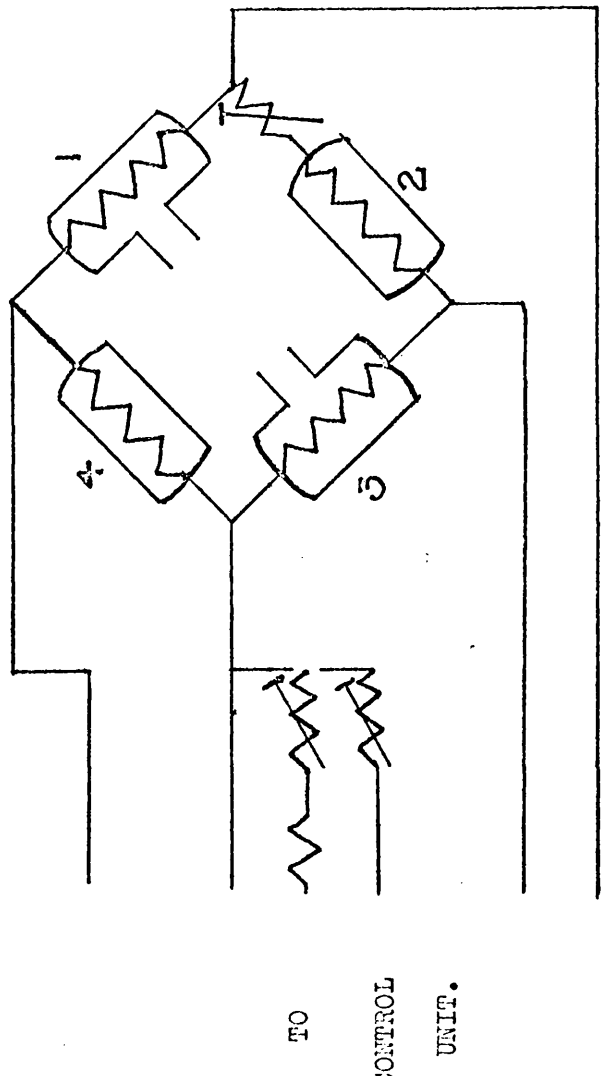
The basic objective of TVA is to measure the rate at which volatile material is evolved from a degrading polymer, at a particular temperature.

The rate measuring instrument in this case is a Pirani gauge. A complete description of the electronic circuitry in the device used in this work is not appropriate to the present discussion, which will be limited to an explanation of the basic principle of operation of a Pirani gauge.

Each gauge head consists essentially of a Wheatstone bridge circuit, constructed of four identical tungsten filaments, each of which is mounted in a glass tube. (Fig. 2,2).

Two of the tubes are hermetically sealed under vacuum, while the others have one end open to the TVA system. For a given voltage across a heated filament, the temperature of the wire, and hence its resistance, depends upon the rate at which heat is conducted away from the filament by the surrounding gas. Since the conductivity of a gas is a function of its pressure, the resistance of the filament will be a function of the pressure in its vicinity.

Filaments 2 and 4, being sealed, are insensitive to



FIGURE(2,2), Wheatstone Network Of Pirani Gauge.

fluctuations in pressure. However, changes in the resistance of filaments 1 and 3 will cause an out of balance current to flow, which can be read as pressure on a meter, or monitored using a suitable recorder. The control unit serves as a source of stabilised d.c. voltage, incorporates a meter for direct read-out of pressure, and provides a suitable output to a recorder of the voltage imbalance in the circuit.

Since the system is under continuous pumping, the pressure above the sample, and therefore the Pirani response, is related to its rate of volatilisation, i.e. the rate of transfer of the volatile products of decomposition from the heated sample to the cold trap.

Recording of Experimental Variables.

Two Pirani gauge outputs were simultaneously recorded throughout an experiment on separate Beckmann single pen Potentiometric Recorders, operating on a 0 to 10 mV. scale, corresponding to the output from the Pirani control unit. At the same time, the output from the thermocouple C was recorded on a Leeds and Northrup single pen recorder (Speedomax H), fitted with a reference junction compensated range card, permitting a direct temperature read-out on chart paper with a 0-600^{o}C. scale. The three recorders were switched on simultaneously at the

commencement of an experiment.

The success of the TVA technique, as for many other modern instrumental techniques, relies greatly on the faith which can be placed on the recorded data. The important parameters in this respect are the recorder pen response and chart speed.

The "gain" and "damping" controls on the recorders were checked periodically, usually requiring no adjustment. Care was taken to ensure that the recorder span (response to input) was correctly set using a potentiometer. (Doran Thermocouple Potentiometer, Denitron Instruments Ltd.).

Chart speed, for both types of recorders, was found to be highly reproducible (less than 5 sec. error in one hour), and the recorders were operated so as to minimise "backlash" in the chart drive mechanism.

When the above precautions were taken, it was possible to obtain reproducible temperature-Pirani output traces, or thermograms, for a particular substance, under given conditions.

Sample Preparation.

The importance of sample form in polymer degradation studies has already been emphasised (Chapter 1, page 14). The area of the base of the degradation tube being approximately 10 sq. cm., the size of sample used in this work (1-100 mg.) could be easily

accommodated as a thin film, fine powder, or in the form of thin slices, without necessitating the use of excessively thick samples.

The normal procedure in this work was to degrade the sample as a thin film, cast directly onto the tube base. This was the preferred practice for a number of reasons:-

(a) The weight of the tube (approx. 140 g.) meant that considerable errors were introduced when weighing, say 20 mg. samples, into the tube. It was obviously difficult and tedious to weigh out precisely the same weight of sample on repeated occasions. The use of a known volume of a solution of the polymer, in order to introduce the sample into the tube, is a more reproducible procedure, since the volume introduced, and the concentration of the solution, can be measured with greater accuracy than is possible using the alternative approach.

(b) With powdered samples, it was found difficult to ensure that the sample did not adhere to the side walls of the tube, and that the sample was distributed evenly on the tube base. Careful film preparation, following the same procedure throughout, ensured a more reproducible sample form.

(c) Providing the solvent is inert, film preparation is less likely to cause prior degradation of the polymer than is the

prolonged grinding process which may be necessary to powder a polymer sample.

The procedure for film preparation was as follows:-

A known volume (usually 1 ml.) of a solution of the polymer of known concentration was pipetted onto the base of the tube. Volatile solvents such as benzene, toluene, acetone, and tetrahydrofuran were removed at room temperature, under a slow stream of nitrogen (containing less than 7 ppm. of oxygen), while the tube was clamped in a vertical position. Less volatile solvents, such as cyclohexanone, were removed under continuous pumping in a vacuum oven, again at ambient temperature. In either case, oxygen was excluded as far as possible during film formation.

The film drying process was continued until the film was clearly free of liquid (normally one-two hours). The tube was then placed in position in the TVA system, and opened to the pumps.

The best vacuum attainable in the apparatus, corresponding to zero Pirani reading (which was equivalent to a "sticking" vacuum on a "Vacustat" gauge), was usually achieved within twenty minutes, providing the residual solvent in the sample was not excessive.

Product Collection.

The products arising from degradation of a sample in the TVA apparatus can be divided into two categories:-

(a) The involatile residue.

(b) The volatile products, which can be further classified into:-

(i) Those products volatile at the temperature of degradation but involatile at room temperature.

(ii) Substances volatile at the temperature of degradation but involatile at liquid nitrogen temperature.

(iii) Products volatile, even at liquid nitrogen temperature.

Category (a), the residue remaining on the tube base, if soluble, was subjected to molecular weight determination. Infra-red or ultra-violet spectroscopy was applied to determine the nature of the functional groups present. Unfortunately, the residue could not be examined without interrupting an experiment.

Products of type b (i), which were found to collect on the upper portion of the degradation tube, at the area cooled by the cooling jacket C (figure 2,1), could be collected for subsequent analysis by wiping this region of the tube with a tissue moistened with a suitable solvent. Solvent extraction of the tissue could give a solution of sufficient concentration to permit an I.R. or U.V. spectrum to be run.

Since the cold jacket was constructed of glass, and therefore transparent, it was often possible to observe the formation of this "cold-ring fraction" during the experiment, especially where the product fraction was coloured. The formation of products in categories (b) (ii) and (b) (iii) was detected by the Pirani gauges. In the case of gauges at E, F or H (figure 2,1), all such products were detectable. A Pirani gauge placed at J detected only substances non condensable in liquid nitrogen, such as methane, hydrogen and carbon monoxide.

Since there was no means of isolating the non condensable products in the TVA apparatus, they could only be identified by using an alternative, closed system such as that described in Chapter 5.

Condensable products were isolated in the cold trap by closing the taps, and distilled into a suitable receiver. Infra-Red and Ultra-Violet Spectroscopy, Mass Spectrometry and Gas-Liquid Chromatography were used to identify the substances concerned.

TEMPERATURE CALIBRATION.

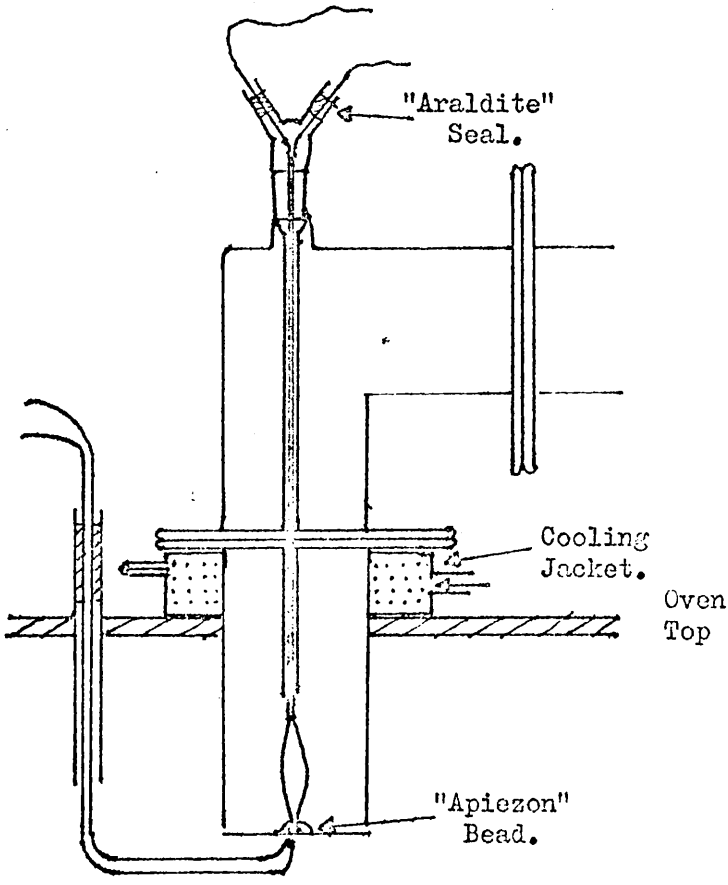
The temperature recorded during an experiment was that of the fixed oven thermocouple C. This was related to the temperature of the tube interior using the experimental arrangement shown in figure (2,3).

The output from the oven thermocouple, and that from a similar thermocouple with the hot junction pressing the interior of the tube base, were simultaneously recorded on separate channels of a Speedomax H "Multipoint" recorder, for nominal heating rates of 2, 5, 10 and 20°C/minute (ten runs at each heating rate).

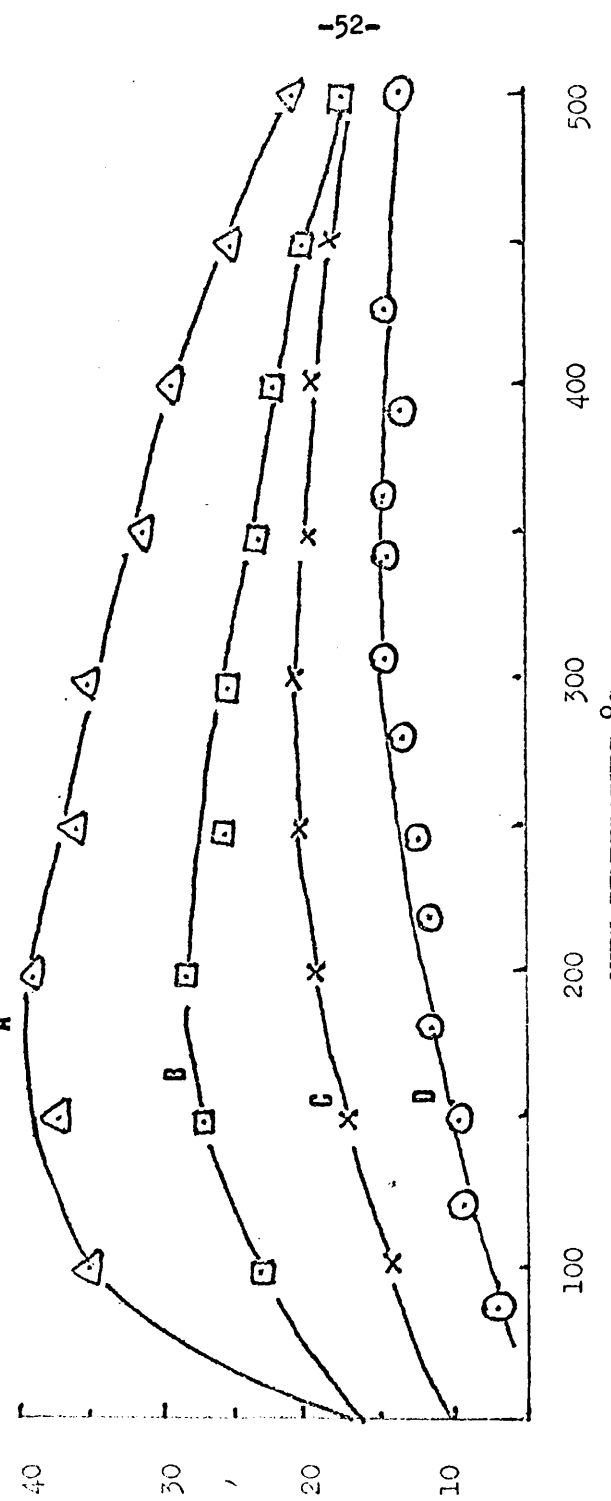
A reference-junction compensated range card was again used in the recorder, eliminating the need for a cold junction in the thermocouple circuit and permitting temperature to be read directly. The temperature recorded by this arrangement was found to be the same as that calculated from the output to a potentiometer of the same thermocouple, with a cold junction (at 0°C.) in the circuit.

The thermocouple junctions were fabricated by fusing the wires together in a hot flame, allowing to cool, and filing the junction bead to a suitable size.

In the case of the interior tube thermocouple, the tip of the junction was deliberately filed flat, and the thermocouple leads made slightly longer than required to reach the tube base, so that downward pressure ensured good contact between glass and junction, when the apparatus was under vacuum. Care was also taken to ensure that the thermocouple leads were well



FIGURE(2,3), Arrangement for temperature calibration



FIGURE(2,4), Temperature differential between oven thermocouple and tube base.

A, at 20°/min., B, at 10°/min., C, at 5°/min., D, at 2°/min.,nominal heating rates.

T A B L E (2,1).

REPRODUCIBILITY OF THERMAL LAG.

No. of Calibrations.	Nominal Heating Rate °C/min.	Temperature differential between oven thermocouple and tube base interior, at the following tube base temperatures, (°C).				
		100	200	300	400	500
10	2	8 ± 1	11 ± 1	14 ± 1	13 ± 1	13 ± 1
10	5	16 ± 2	19 ± 1	19 ± 1	19 ± 1	17 ± 1
10	10	26 ± 2	27 ± 2	24 ± 2	21 ± 1	17 ± 2
10	20	38 ± 4	37 ± 4	32 ± 4	27 ± 3	18 ± 3

T A B L E (2,2)

REPRODUCIBILITY OF HEATING RATE.

No. of Calibrations.	Nominal heating rate °C/min.	Time taken (min.) for the tube base to pass between the following temperatures (°C). 100	200	300	400	500
10	2		46 ± 2	44 ± 1	44 ± 1	47 ± 3
10	5		20.0 ± 0.3	18.5 ± 0.5	17.7 ± 1.2	18.8 ± 1.2
10	10		9.8 ± 0.1	9.5 ± 0.3	9.5 ± 0.2	10.3 ± 0.4
10	20		4.8 ± 0.2	4.7 ± 0.2	5.0 ± 0.2	6.6 ± 0.6

separated. This thermocouple junction was surrounded at the point of contact between glass and metal by a small bead of Apiezon "L" grease, to improve thermal contact, and to simulate molten polymer. The grease required to be replaced after each run, since it volatilised slowly during the experiment.

Chromel-alumel thermocouples were found to be more satisfactory than copper-constantan. The latter oxidised perceptibly, and the junctions had a tendency to break. By contrast, the chromel-alumel couple was robust, and the performance unimpaired by continuous use over two and a half years.

Results and Significance of Temperature Calibration.

In any TVA experiment, the oven thermocouple registers a higher temperature than is actually present in the tube interior. The thermal lag, which is a function of temperature, heating rate, and position of the oven thermocouple, is caused by the insulating effect of the Pyrex glass, and heat losses from the tube to the cooling jacket.

For similar reasons, it must be expected that the heating rate of the tube base will differ from that of the oven, i.e. the oven, not the sample, is temperature programmed.

Temperature Differential.

The temperature differential between oven and tube thermocouples is plotted as a function of temperature, and heating rate, in figure (2,4). It should be emphasised that this temperature lag plot is unique for a particular degradation tube, and TVA apparatus.

It is evident that the differential increases markedly for increasing heating rate. Somewhat unexpectedly, it does not rise with increasing temperature, but passes through a maximum, the position of which depends on heating rate.

The reproducibility of lag for various heating rates is summarised in Table (2,1). The faster is the heating rate the greater is the uncertainty in temperature measurement, but for heating rates below $10^{o}/$minute, the reproducibility of lag is excellent.

Heating Rate.

The reproducibility of heating rate, as experienced by the tube interior, was also tested, the results being shown in Table (2,2). Fluctuations in heating rate, amounting to 5% in some cases, are evident, and as expected, the heating rate at the tube interior is different from the nominal heating rate. Unfortunately, it is not possible to compare these results with

those obtained in TG or DTA systems, owing to the lack of published data.

However, these small fluctuations in heating rate did not affect appreciably the reproducibility of the thermograms obtained at any nominal heating rate. Although thermograms are dependent on heating rate, a change of heating rate of 5% would only cause the thermogram to be shifted by 1 or 2° on the temperature scale (see Chapter 3).

The effect of preheating the tube at 50°C for thirty minutes before allowing the programme to commence was also examined. While the thermal lag was similar to the value observed in the absence of preheating, the reproducibility of heating rate was slightly worsened.

When temperature calibrations were carried out without the tube being continuously evacuated, it was found that the lag increased. This could be due to the glass-metal contact not being as effective as it is under vacuum, when the thermocouple is held firmly down by lid D, or could be due to increased heat loss from the tube by convection.

Thermal Effects During Degradation.

(a) During polymer degradation, heat changes occur, which might alter the temperature of the sample to a value different

from that of the tube base, or the temperature of the tube base to a value different from that experienced in calibration.

Experiments were therefore conducted to determine the importance of these factors. Temperature calibration experiments were carried out, as before, but with polystyrene samples of 50, 100 and 150 mg. on the tube base, in addition to the Apiezon bead. It was found that the thermal lag in the presence of such samples was unchanged from the original value, irrespective of whether the polymer was in the form of a thin film, or fine powder.

This result is not unexpected. The large mass of the tube (140 g) by comparison with that of the sample, means that the thermal capacity of the tube will be sufficiently great to ensure that the thermal effects, which are undoubtedly present during polymer decomposition, will have little influence on the temperature of the tube base.

Furthermore, in normal operation, the sample under investigation is thinly distributed over the large area of the tube base (10 sq. cm.). Assuming that the contact between polymer and glass is reasonably good, the temperature of the sample can be assumed to be the same as that of the tube base, that is, thermal gradients within the sample should not be a serious problem.

This should be contrasted with the situation which is present in many TG and DTA systems, in which massive polymer samples are accommodated in small crucibles, leading to large thermal gradients within the sample, and making the accurate measurement of sample temperature extremely difficult.

ALTERNATIVE TEMPERATURE CALIBRATION METHODS.

The twin thermocouple method of calibration was time consuming and required repetition for each tube used. Efforts were therefore made to find an alternative means of calibration.

(1) Melting Point Method.

To check the accuracy of the previous method of calibration, melting point determinations were carried out on lead wire and tin foil of high purity. The wire, or the foil, cut as a thin strip, was embedded in Apiezon grease on the base of the tube, and connected to a circuit containing a constant voltage source (a potentiometer), the connecting wires passing through a Y-piece B 14 air leak of the type used to accommodate the thermocouple wires in (figure 2,3). The potentiometer was adjusted so as to give sufficient output to give half scale deflection on a Beckman recorder in the circuit. In a similar manner to the tube thermocouple, slight downward tension was applied to the test sample, when the apparatus was under vacuum. Melting of the sample, and breaking of the circuit, was indicated by a sudden

drop to zero deflection of the recorder trace.

By this method, values of 325 ± 5°C and 232 ± 1°C were obtained for the values of the melting points of lead and tin respectively (literature values 327°C and 232°C respectively), thus confirming that the temperature of the tube base was that indicated by the calibration experiments.

While these experiments did confirm that the original calibration method was reliable, it was not sufficiently general in application to supplant the former.

(2) Calibration by Peak Maxima of Model or Standard Substances.

As will be shown in subsequent chapters, the TVA thermogram of a substance may contain one or more "peaks" often with sharply defined maxima and minima. The position on the temperature scale of these features is characteristic for a particular substance, at a given heating rate. If a substance, or mixture of substances could be found, with a sufficiently large number of sharp peaks in the temperature range of interest, 200°C to 500°C, it would be possible to calibrate a new tube or a new TVA system by comparing the thermogram obtained with standard thermograms obtained on other units.

This possibility was examined, and both polymeric and inorganic samples were run, and positions of peak maxima

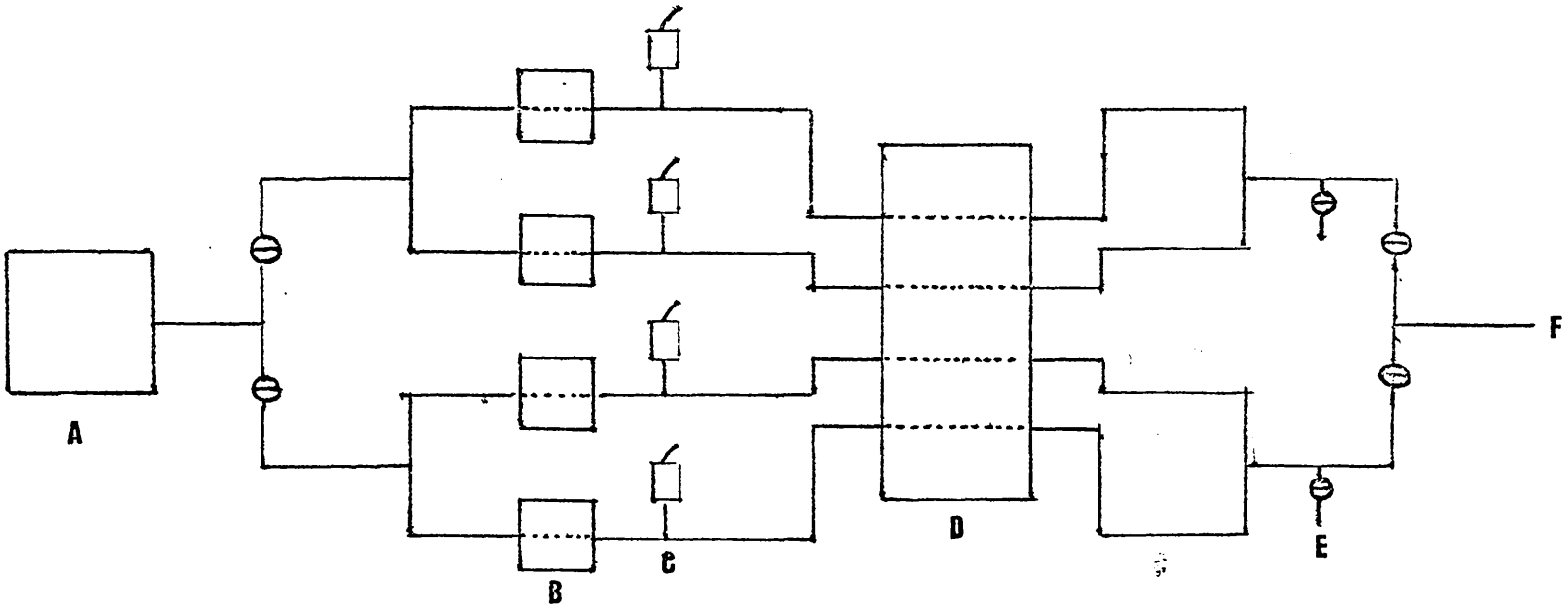
compared with those obtained on other TVA systems. Although the agreement between the results from the three different units was within 8° (at 10°/min), it was decided that this method of calibration was not yet sufficiently general to supplant the more direct method using two thermocouples.

TVA WITH DIFFERENTIAL CONDENSATION. (55)

An alternative type of TVA apparatus was also used in this work, and is shown on figure (2,5) in diagrammatic form. In principle, this apparatus was the same as that previously described, Pirani gauge heads being used to register the transfer of degradation products from heated sample to a liquid nitrogen trap. Four equivalent routes were provided along which the product stream could pass, with a secondary cold trap in each. A Pirani gauge head was placed between each secondary trap and the common trap.

In normal usage, each of the secondary cold traps operated at four different temperatures, usually 0°, - 45°, - 75° and 100°C respectively.

Only substances which can pass through the appropriate trap can be registered by the Pirani gauge. Where the distilling substance is non condensable at - 100°C, then obviously it will be non condensable at temperatures greater than - 100°C. The



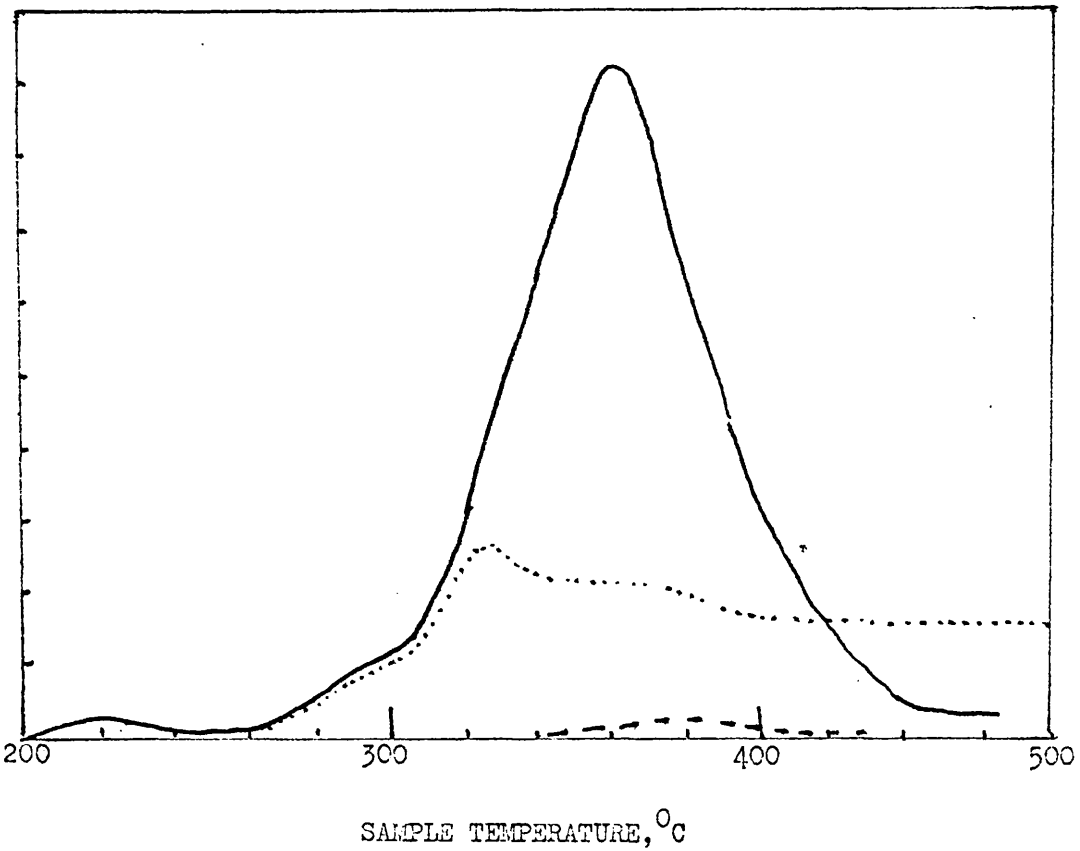
FIGURE(2,5) Differential Condensation TVA Apparatus.

A, Heated Sample.
B, Secondary Cold Trap.
C, Pirani Gauge Head.
D, Common Cold Trap
E, Receiver for Products
F, To Pumping System.

output from each Pirani is then the same. In the thermograms of PVC and polychloroprene, where the major product (hydrogen chloride) is not condensed at - 100°C, the four Pirani traces are coincident.

For poly (methyl methacrylate), the traces at 0° and - 45° are coincident, while that at - 100°C remains on the base line. The trace at - 75°C, however, attains an equilibrium value of Pirani output, characteristic for methyl methacrylate, as the monomer slowly distills from the secondary to the common trap. Such a thermogram is shown on figure (2,6). A list is given in Table (2,3) showing the behaviour in the differential condensation apparatus of a few substances. As can be seen, several substances exhibit a "vapour pressure" at - 75°C. However the value of Pirani output corresponding to this slow distillation is different for each, and can be useful in identifying the substance concerned.

This modification of the original principle can yield considerable information concerning the nature, and relative proportions of the volatile products. Eventually, it will probably supersede the original TVA method.



FIGURE(2,6), A DC-TVA Thermogram for a Sample of Poly(methyl methacrylate), (F.R.I.) (At a Heating Rate ≈ 10°/min.)

— — — — — Pirani output from a gauge head placed after a cold trap at -100°C

..... Output from similar gauge, trap at -75°C

——— Outputs from gauges after cold traps at 0°C, and -45°C

T A B L E (2,3)

BEHAVIOUR OF VARIOUS SUBSTANCES IN THE DIFFERENTIAL CONDENSATION APPARATUS.

C = Fully condensed (Pirani output for this trap temperature = 0).

NC = Not condensed (Pirani output at trap temperature in question = Pirani output at any higher trap temperature).

VP = Material partially condensed by secondary trap, so that the slow distillation to the liquid nitrogen trap is registered as a steady Pirani output.

SUBSTANCE.	TRAP TEMPERATURE °C.			
	0	-45	-75	-100
Acetic Acid.	NC	VP	VP	C
Carbon Dioxide.	NC	NC	NC	NC
Carbon Monoxide.	NC	NC	NC	NC
Hydrogen Chloride.	NC	NC	NC	NC
Isobutene.	NC	NC	NC	NC
Methane.	NC	NC	NC	NC
Methyl Chloride.	NC	NC	NC	NC
Methyl Methacrylate.	NC	NC	VP	C
Methyl Vinyl Ketone.	NC	NC	NC	C
Alpha-Methyl Styrene.	NC	VP	C	C
Styrene.	NC	NC	VP	C
Water.	NC	NC	VP	C

Notes. (1) Value of Pirani output, for substances of VP type is characteristic for a given material, although it is unique for a particular DC-TVA apparatus.

(2) If the rate of production of a VP type material is such that the characteristic Pirani output is not attained, then the substance behaves as if it were non-condensable.

CHAPTER THREE.

FACTORS AFFECTING THE TVA THERMOGRAM.

DESCRIPTION OF A TVA THERMOGRAM.

In this chapter the factors which have been found to influence a TVA thermogram are classified, and their relative importance assessed. Obviously, the significance of these factors must be established before thermograms can be clearly interpreted.

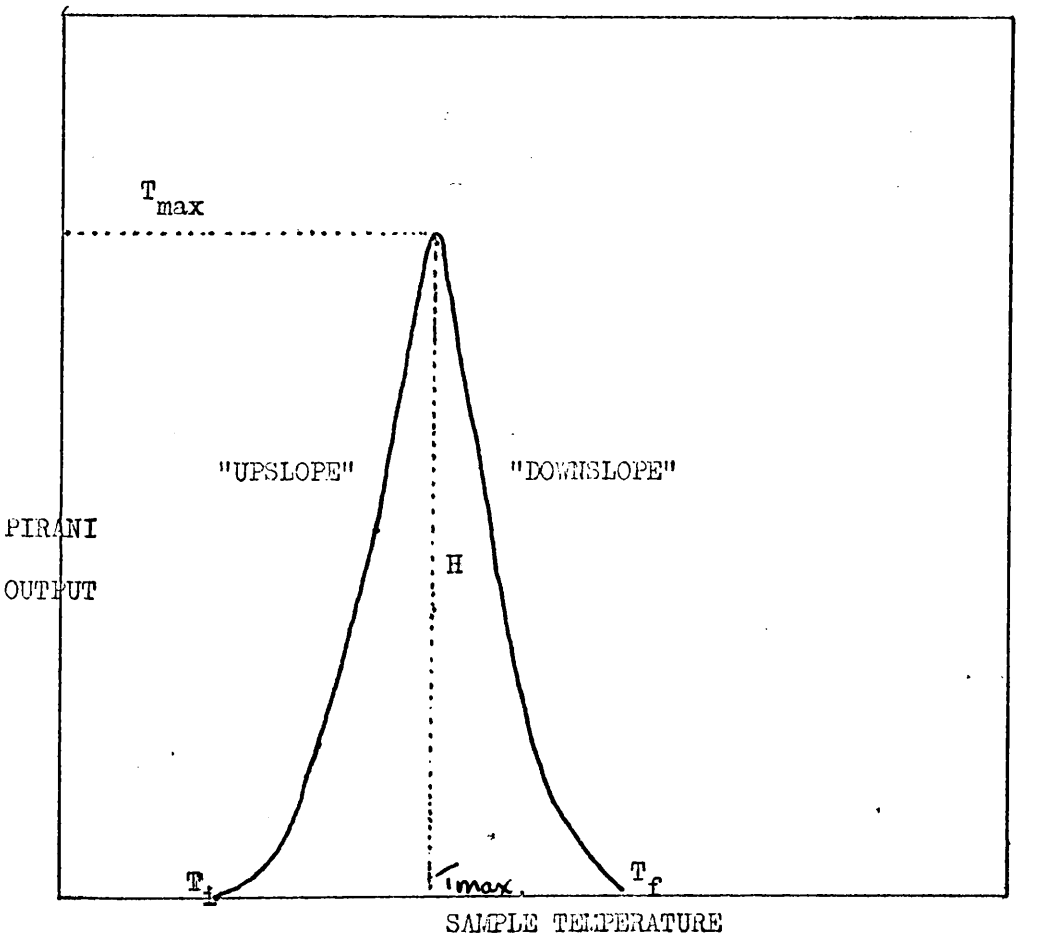
An idealised thermogram, representing a single stage decomposition process is shown in figure (3,1). Pirani output is plotted against sample temperature. The significant features of the thermogram can be defined:-

(1) T_i and T_f, the temperatures at which volatilisation becomes, and ceases to be detectable, respectively.

(2) T_{max}, the temperature at which the Pirani output attains a maximum value.

(3) H, the value of the Pirani output at T_{max}, usually referred to as peak "height".

(4) The "shape" of the thermogram, which is less easily defined, being determined by the manner in which the Pirani output changes as a function of temperature on the "upslope" and "downslope" of the thermogram.



FIGURE(3,1), Significant features of a TVA Thermogram.

In many cases, TVA thermograms are less simple than the example shown in figure (3,1), often consisting of several peaks which may overlap. In general, however, the position of a peak can be defined by the T_{max} value, which is often characteristic of the decomposing substance.

CLASSIFICATION OF FACTORS WHICH AFFECT A TVA THERMOGRAM.

The factors which must be taken into consideration when interpreting a TVA thermogram can be classified into three main categories:-

(a) Apparatus Variables, concerning the effect which the manner of operation and construction of the TVA apparatus can have upon the TVA thermogram.

(b) Sample Variables, concerning the influence of sample weight, form, and history on the TVA thermogram for a particular substance.

(c) Kinetic Parameters, concerning the relationship between the chemical kinetics of the decomposition process, and the resultant TVA thermogram.

In this chapter, the importance of each of these factors will be discussed in turn, and where possible, the relationship between a TVA thermogram and the results from other methods of studying polymer decomposition will be examined.

APPARATUS VARIABLES.

FACTORS AFFECTING THE SENSITIVITY OF THE PIRANI GAUGE.

(a) The Nature of the Material Passing the Gauge Head.

The operation of the Pirani gauge has already been described (Chapter 2, page 42). In normal operation, the TVA apparatus is continuously evacuated. Consequently, the pressure in the system and therefore the response of the Pirani gauge, will be a function of the rate at which material passes the gauge head. Assuming the transfer of material from sample to cold trap is rapid, the rate of passage of degradation products past the gauge head will be the same as the rate of volatilisation of the heated sample. The evidence presented subsequently in this chapter will show that this is indeed the case, under normal conditions of operation of the apparatus.

Unfortunately, however, the absolute rate of degradation of the sample cannot be directly computed from the Pirani gauge output. One reason for this is the different response which the gauge has to the same pressure of different substances. Since the rate of heat loss of the heated filament is dependent upon the thermal conductivity of its environment, the response of the gauge will be a function not only of the rate of flow, but also of the thermal conductivity of the degradation products.

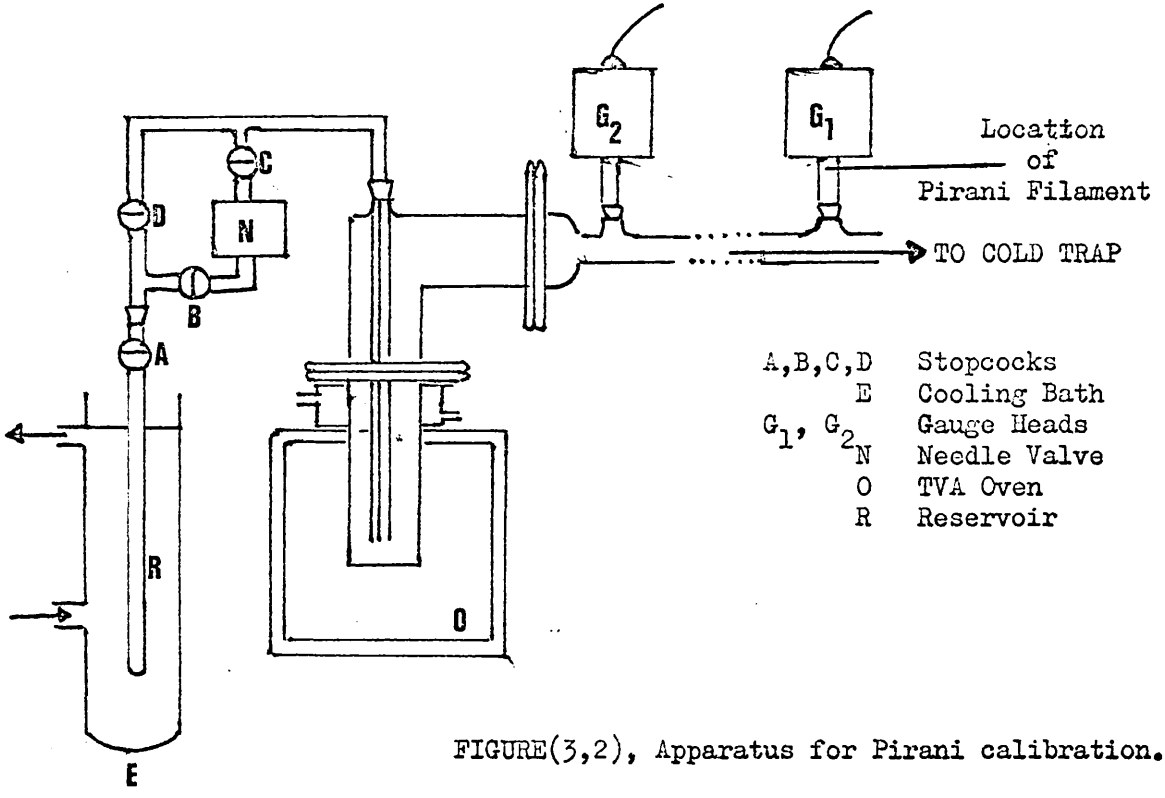
Calibration of Pirani Gauge.

The response of the Pirani gauge to various substances was

tested using the apparatus in figure (3, 2). The liquid under examination, after thorough degassing, was distilled from the uniform bore reservoir R, past the gauge heads G_1 and G_2, to the cold trap. The rate of flow of vapour was controlled by means of the needle valve and the flow was directed to the base of the degradation tube, as shown, in order to simulate the route taken by the degradation products.

At the beginning of an experiment, the stopcocks A, B and C were opened, and the needle valve adjusted to give the required rate of distillation (i.e. the required Pirani response). Once the outputs from G_1 and G_2 had become steady, i.e. the rate of transfer of liquid was uniform, the level of the meniscus was noted, and the chart drives of the recorders were activated. Distillation was allowed to proceed at this Pirani output for at least one hour, low flow rates requiring longer distillation times to give a reasonable change in the height of the meniscus. At the end of the experiment, the distillation time and level of the meniscus were noted, and the recorder drives were stopped. The experiment was then repeated, for a different steady distillation rate, the value of meniscus drop, and time of distillation being noted in each case.

Care had to be taken to ensure that all the liquid emerging from the reservoir distilled to the cold trap. This was achieved



FIGURE(3,2), Apparatus for Pirani calibration.

by means of the cooling bath E, through which mains cold water was continuously passed. The temperature of the bath being below room temperature, the vapour was prevented from condensing within the system.

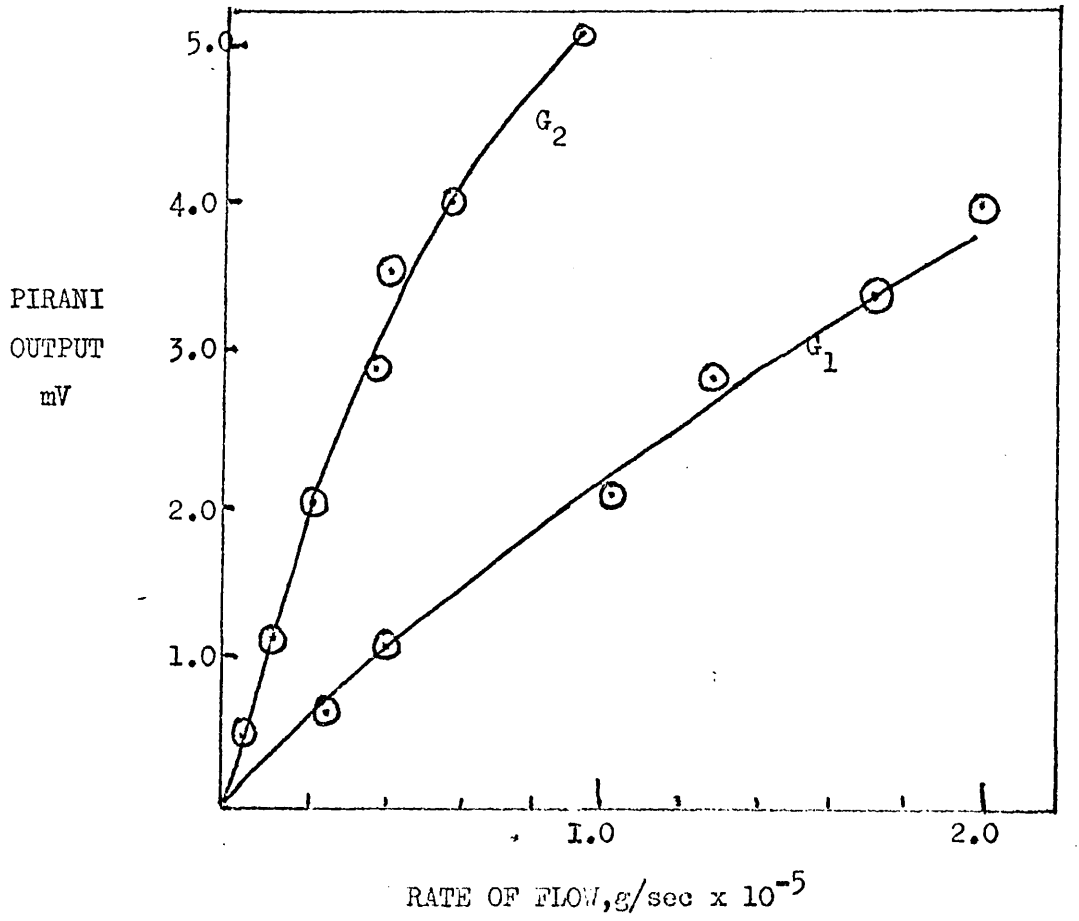
The rate of flow of vapour during the course of a calibration was determined by calculating the volume drop of the liquid in the capillary over the period of distillation. The mass of liquid transferred in the time interval was then determined by applying the appropriate density correction for the temperature of the distilling liquid, which was assumed to be that of the cold bath. In this way, calibration data were collected for water, methyl methacrylate, styrene and acetic acid.

It was found necessary to ensure that the level of liquid nitrogen in the cold trap was kept topped up during the distillation process, since a fall in the liquid nitrogen level caused a perceptible upward drift in Pirani output for the same flow rate. This phenomenon will be explained in the next section.

Results of Calibration Experiments.

A typical calibration plot, for the distillation of water, is shown in figure (3,3). Two features are apparent in this, and the other calibration plots obtained:-

(1) Although the Pirani response is approximately linear within



FIGURE(3,3), Pirani calibration for water
Relative positions of gauge heads as in Figure(3,2)

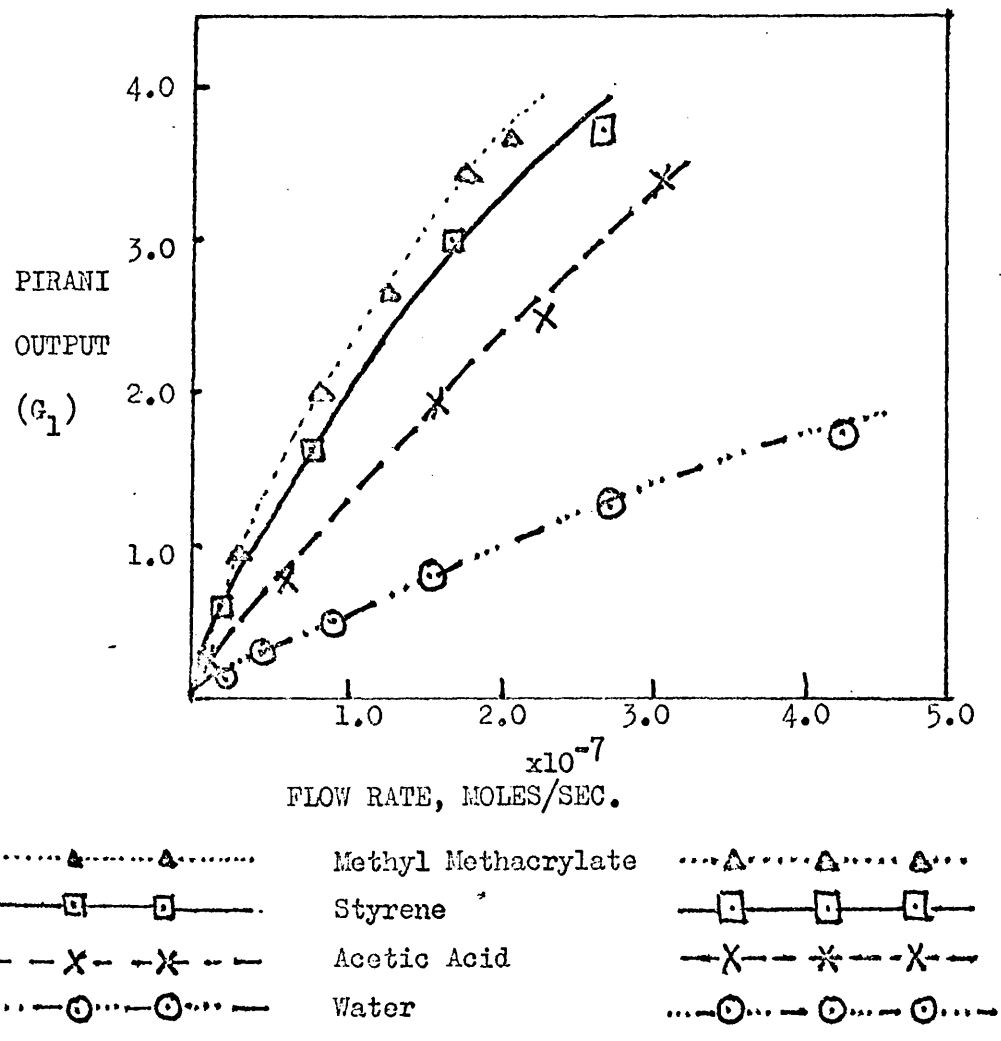
the error of the calibration, up to 2 mV for G_2, the output is essentially non-linear with flow rate thereafter. The curvature of the plot is such that the Pirani becomes progressively less sensitive as the rate of distillation of liquid rises.

(2) The response from G_2, the gauge furthest from the cold trap, is consistently greater than that from G_1. This is a consequence of the pressure gradient which will exist between the degradation tube and the cold trap where, since the material has condensed, the pressure will be extremely small. The effect of the location of the gauge head on the sensitivity of the Pirani gauge is discussed more fully in a later section of this Chapter.

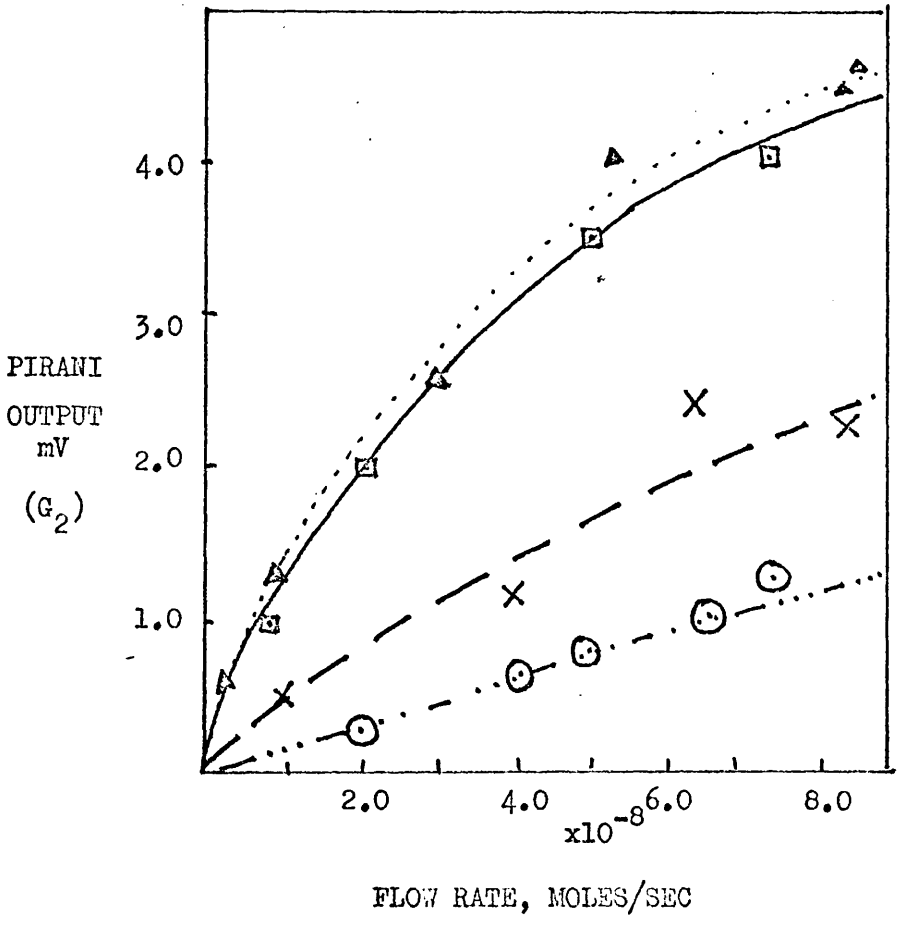
The response of G_1 and G_2 to the various substances used in calibration is summarised in figures (3,4) to (3,7), on both a molar and mass transfer basis.

The response per unit mole, over the range of Pirani output considered, increases in the order water, acetic acid, styrene, methyl methacrylate.

The response per unit weight of the various materials is more nearly comparable. Below 3 mV output on G_2, water, methyl methacrylate and styrene give responses which are similar, although greater than that for acetic acid. At outputs greater than 5 mV,



FIGURE(3,4), Response of Pirani gauge to the same flow rate of different substances, on a molar basis (G_1)



FIGURE(3,5), Response of Pirani gauge to the same flow rate of different substances, on a molar basis (G_2)

For key to representation of experimental points, see Figure(3,4)

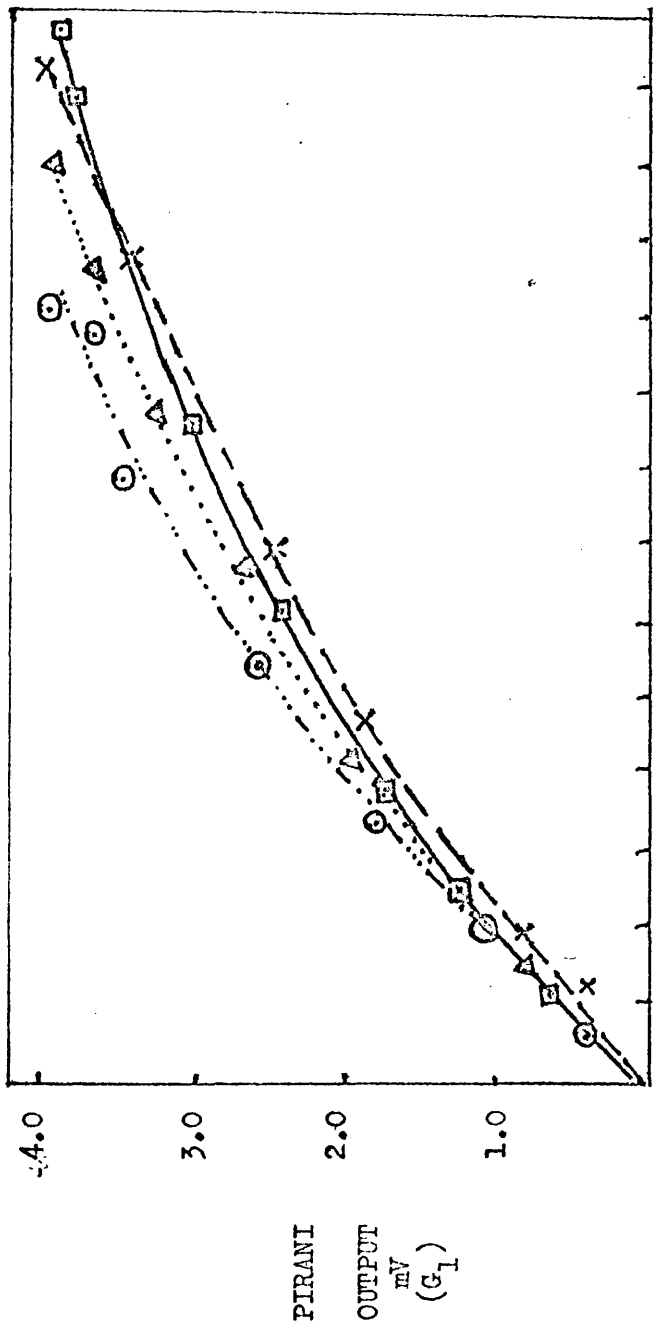
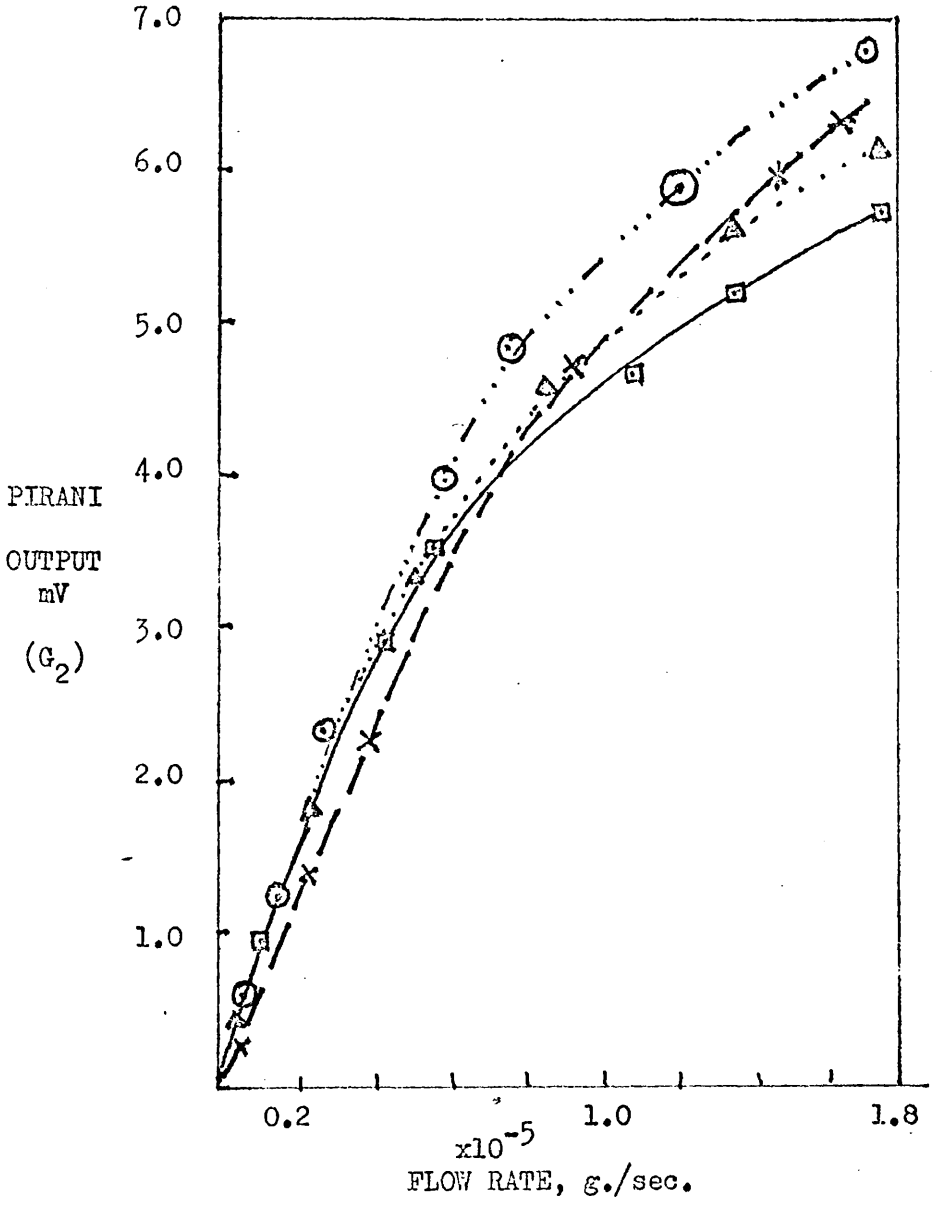


FIGURE (3,6), Response of Pirani gauge to the same flow rate of different substances, on a weight basis. (G_1)

For key to the representation of experimental points, see figure(3,4)



FIGURE(3,7), Response of Pirani gauge to the same flow rate of different substances, on a weight basis (G_2)

For key to the representation of experimental points, see figure(3,4)

the order of increasing output is styrene, methyl methacrylate, acetic acid and water.

Not only the response of a single Pirani, but the relative responses G_2 : G_1, were found to be unique for the particular substance distilling.

This is shown in table (3,1) in which the output from head G_2 is tabulated, for various substances, at fixed G_1 outputs. Clearly, the ratio response G_2 : response G_1, is a function both of the flow rate and the distilling substance.

The Significance of Calibration Results.

The calibration plots establish that the Pirani output can only be described as linear with the rate of volatilisation of the sample where the output is low (below 2 mV). The relationship between rate of degradation and Pirani output is unique for the substance evolved, and the location of the Pirani in the system. In order to obtain absolute values for the rate of the reaction, it is necessary to identify the substance concerned and apply a suitable calibration technique. Where a complex mixture of products is evolved during polymer degradation, however, the difference in the Pirani response towards the various constituents of the mixture makes it impossible to calibrate the gauge head by the method described above. In such cases it may be possible to adopt an

T A B L E (3,1).

RELATIVE PIRANI OUTPUTS FOR VARIOUS SUBSTANCES.

Output from G_1 (mV)	Output from G_2 (mV) for undernoted substances.			
	WATER	STYRENE	ACETIC ACID	MMA.
0.5	1.64	1.42	1.37	1.41
1.0	2.94	2.60	2.91	2.78
1.5	4.13	3.72	4.2	3.88
2.0	4.96	4.48	5.08	4.75
3.0	6.16	5.64	6.48	5.92
4.0	6.96	6.48	-	-

alternative, although somewhat less satisfactory calibration technique, described in a later section of this Chapter.

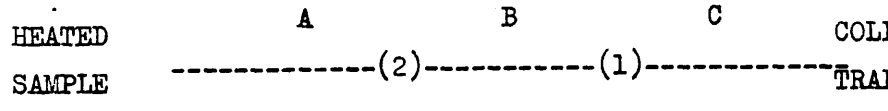
(b) Location of the Gauge Head.

Position of Gauge Head, Relative to Sample and Cold Trap.

The different responses of G_2 and G_1 to the same flow rate of vapour, as observed during calibration experiments, is a clear indication that the sensitivity of the Pirani gauge depends upon its position in the TVA system.

Experiments were conducted in order to test further the relationship between Pirani response and the location of the gauge head, relative to the cold trap and the sample tube.

The TVA system can be represented as shown below:-



where (2) and (1) represent G_2 and G_1 respectively, and A is the distance between the sample and the point of attachment of G_2, and so on.

The effect on the sensitivity of G_2 and G_1 of altering the distances A, B and C, was examined. This was done by degrading the same weight of polymer, at the same heating rate, but with different lengths of tubing in sections A, B and C, and comparing the thermograms obtained from gauges G_2 and G_1,

under each new set of conditions.

The effect on Pirani sensitivity was found to be as follows:-

(1) An increase in the length of A caused the sensitivity of both G_2 and G_1 to fall.

(2) An increase in B caused the sensitivity of G_2 to rise, while that of G_1 fell slightly.

(3) An increase in C caused the sensitivity of both G_2 and G_1 to rise.

This experiment, together with the calibration experiments, established that the further a gauge head was from the cold trap, the more sensitive it became to a given flow rate. Conversely, the more distant the gauge head was from the heated sample, the smaller the output to the recorder for the same flow rate.

In the light of this evidence, it would be tempting to assume that the pressure, or Pirani response P, at any point between the heated sample and the trap could be described by an expression of the type (a):-

$$P = P_S \times \text{function} \left(\frac{\text{distance between gauge head and trap}}{\text{distance between gauge head and sample}} \right) \quad (a)$$

where P_S = pressure immediately above the sample.

However, this function does not adequately describe the situation as the following argument will show.

Assuming (a) to hold, we have

$$P_{(2)} = P_s \times \text{function } \left(\frac{B + C}{A}\right);$$

$$P_{(1)} = P_s \times \text{function } \left(\frac{C}{A + B}\right).$$

Now as A tends to 0, $P_{(2)}$ should tend to P_s, that is $\left(\frac{B + C}{A}\right)$ should tend to unity. However, the function $\left(\frac{B + C}{A}\right)$ tends to infinity. Similarly, as $(A + B)$ tends to zero $\left(\frac{C}{A + B}\right)$ tends to infinity. Expression (a) must therefore be incorrect.

An alternative function can be used to describe P, however:-

$$P = P_s \times \text{function } \left(\frac{\text{distance between gauge head and trap}}{\text{distance between sample and trap}}\right) \quad (b).$$

We have $P_{(2)} = P_s \times \text{function } \left(\frac{B + C}{A + B + C}\right);$

$$P_{(1)} = P_s \times \text{function } \left(\frac{C}{A + B + C}\right).$$

Now $P_{(2)}$ tends to P_s as A tends to zero, while $P_{(1)}$ tends to P_s as $(A + B)$ tends to zero.

If the distance B is increased by L, we have $P_{(2,L)} = P_s \times$ function $\left(\frac{B + L + C}{A + B + L + C}\right)$, while $P_{(1,L)} = P_s \times \text{function } \left(\frac{C}{A + B + L + C}\right)$.

It can be shown that $\left(\frac{B + L + C}{A + B + L + C}\right)$ is greater than $\left(\frac{B + C}{A + B + C}\right)$, hence $P_{(2,L)}$ is greater than $P_{(2)}$. Similarly, $P_{(1,L)}$ is less than $P_{(1)}$.

The effect of increasing the distance B is thus explained satisfactorily by expression (b).

The level of liquid nitrogen in the cold trap in effect defines the position of the cold trap relative to the sample. The lower the level, the greater is the sample-trap distance. The upward drift of the Pirani output as the liquid nitrogen level fell during calibration experiments, is thus explained.

Position of Pirani Filament.

As previously discussed, the output from the Pirani gauge at any instant, is a function of the pressure of volatile material at the Pirani filament. It can be seen from figure (3,2) that the Pirani filament is not located in the direct route which the product stream must take from sample to traps, but is situated a short distance away from the actual point of insertion of the gauge head. It might be the case, therefore, that the pressure recorded by the gauge is different from that which exists in the TVA system, at the point of attachment of the gauge head.

The effect of increasing the length of the socket at which the gauge head was connected to the system was therefore investigated.

Even when the socket was extended by a six foot length of tubing, no detectable change in the TVA thermogram was observed, when compared with thermograms obtained using the original socket.

Although a pressure gradient is present in the direct route between sample and cold trap, it would appear that no significant

gradient is present in the side arm containing the Pirani filament. Thus we can reasonably assume that the pressure at the filament is the same as the pressure in the system at the point of location of the socket.

Speed of Pirani Response and Location of Pirani Gauge.

It might be supposed that the more distant a gauge head is from the heated sample, the later it will be in recording a particular event. The time taken for the Pirani to respond to the passage of volatile material was therefore tested in two ways:-

(1) Using the apparatus illustrated in figure (3,2), it was found that opening the reservoir tap caused an immediate deflection of the Pirani recorder trace. Attempts to time the interval which elapsed between opening the tap, and the moment of departure of the recorder trace from the base line, showed that it was no greater than the "dead time" of the recorder, irrespective of whether the output was that from G_1 or G_2.

(2) Comparison of the Tmax values, as recorded by G_1 and G_2, showed that the heads recorded the same event simultaneously, within the limits of experimental error. This was true both when the TVA system had its usual dimensions, and also when an additional six foot length of tubing was interposed between G_1 and G_2.

Experiments of the type described above indicate that during normal operating conditions of the TVA apparatus, the output from a gauge head placed at any point between sample and cold trap is a function of the rate of decomposition of the sample, at the time the measurement is made.

(c) Efficiency of Product Removal.

During the normal operation of a TVA apparatus, the sample is continuously evacuated, both by cold traps and the vacuum pumps, so that products are removed from the reaction zone as they are formed. It has been shown that under these conditions, the Pirani response is a function of the absolute rate of degradation of the sample. If, however, the products were not continuously removed in this manner, and the TVA thermogram was obtained when the sample was heated in a closed system, without a cold trap, the shape assumed by the thermogram would be similar to that of a TG thermogram, such as that shown in figure (1,1), (page 23). That is, the Pirani output would be proportional to the extent, rather than the rate of volatilisation of the sample.

Since the presence of cold trap and pumps can influence the nature of the Pirani output so profoundly, it might be expected that the shape observed for a TVA thermogram under normal operating conditions, would be influenced by the efficiency

with which products are condensed, or pumped away. Important factors in this context are the position and temperature of the cold trap, and the dimension of the vacuum system. For non-condensable products, the efficiency of the pumps themselves is also important.

Importance of Cold Trap.

The results of McNeill [66] suggest that for condensable products, the lower is the temperature of the coolant surrounding the cold trap, the more efficiently the products are removed from the reaction zone (i.e. for a gauge head placed between sample and cold trap, the Pirani response, for the same rate of sample volatilisation, increases for increasing trap temperature).

The fact that the level or temperature of coolant at the cold trap, or the position of the trap relative to the heated sample can influence the response of the gauge to a given flow rate, is a clear indication that the main "pumping force" in the system, for condensable products, is the cold trap, rather than the diffusion or rotary pumps.

This has been further demonstrated by McNeill and Mohammed[67], who have obtained TVA traces for polystyrene samples, with the usual cold trap, but with the system isolated from the pumps. These were virtually identical to thermograms obtained under the

continuous action of the pumps.

Dimensions of Vacuum System.

Probably the most important geometrical factor determining the pumping efficiency is the internal diameter of the tubing used to connect the heated sample to the cold trap. It is well known that if the internal bore of the tubing used in a vacuum system is reduced, the rate at which the system can be "pumped down" is also reduced.

The normal bore of tubing used in the TVA apparatus shown in figure (2,1) was 15 mm. or greater. The effect of placing a constriction in the system was examined by replacing a short length (6 in.) of the glass tubing between the point of insertion of G_2 and the cold trap by tubing of 3 mm. internal diameter. The effect of this was to cause the Pirani output at any point on the thermogram as recorded by G_2, to increase, for the same size of sample [67],

It has also been observed [67] that the Tmax of the thermogram, in the presence of such a constriction, is displaced to slightly higher temperatures (approx. 3°).

The increase in Pirani output, and the delay in Tmax, are probably attributable to the rate of product removal having been impaired by the constriction. Thus although the rate of

sample decomposition is probably not altered by the constriction, there is an alteration in the pressure exerted in the system by the products.

The experiments conducted in the absence of the constriction clearly establish, however, that in the normal operation of the TVA apparatus, the efficiency of product removal is such that the Pirani response at any point on a TVA thermogram is directly related to the rate of sample volatilisation.

THE EFFECT OF HEATING RATE ON THE TVA THERMOGRAM.

The effect of heating rate on the TVA thermograms of polystyrene, poly (methyl methacrylate), and poly (vinyl chloride) was investigated by degrading the same weight of material at different nominal heating rates, and comparing the resultant thermograms.

For 15 mg. samples of polystyrene NBS 706, at nominal heating rates of 2, 5, 10 and 20°C/min, the following changes in the appearance of the thermogram were observed:-

(a) As the heating rate increased, the position on the temperature scale of the rate maximum shifted to higher temperatures.

(b) As the heating rate increased it was found that the rate of degradation, i.e. Pirani output, increased at Tmax.

(c) Two temperatures, T_1 (370°c) and T_2 (450°c) were chosen

such that they were always on the upslope, and downslope, of the thermogram, respectively. It was found that increased heating rate caused the Pirani output at T_1 to fall (from 2.0mV at 2°/min to 0.9mV at 20°/min). For T_2, however, increasing heating rate caused the rate to increase (0.3mV at 2°/min to 5mV at 20°/min). Similar changes were observed in the thermograms of the other polymers.

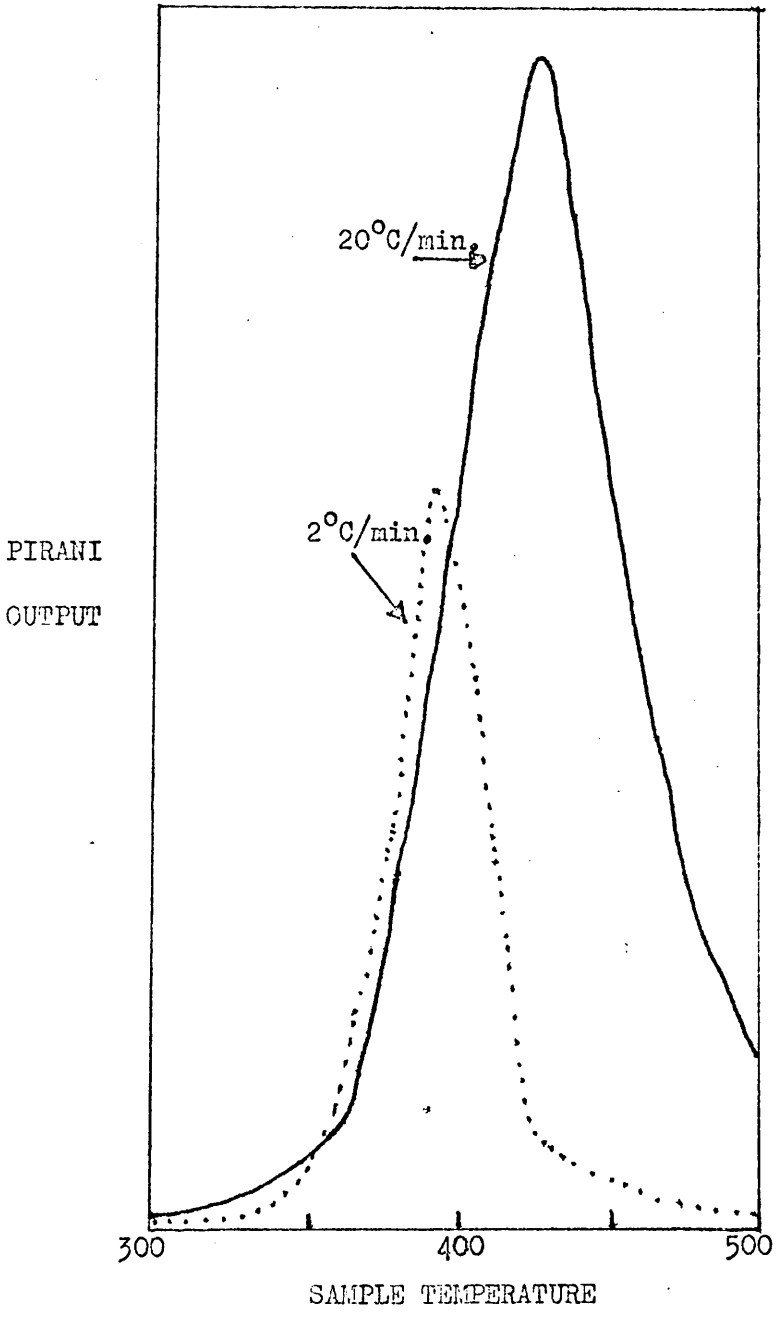
Two thermograms for NBS 706, at different heating rates, are plotted out on figure (3,8) showing up these factors. The displacement of the peak to higher temperatures can be shown to be a direct consequence of the kinetic requirements of the thermogram (see figure 3,7).

Where possible, polymer thermograms should be obtained at different heating rates. Although slow heating rates give better resolution of overlapping reactions, faster heating rates point up slow reactions, or those involving little volatilisation. For example, the second stage of decomposition of poly (vinyl chloride) is much more evident at faster heating rates, for the same weight of sample.

SAMPLE VARIABLES.

SAMPLE WEIGHT OR THICKNESS AND THE TVA THERMOGRAM.

It must be established in what manner a TVA thermogram



FIGURE(3,8), Effect of Heating Rate on TVA Thermogram of Polystyrene,NBS706.

depends upon the initial weight of the polymer sample. When a sample is prepared as a film, cast from a solution of known concentration, the thickness of the film will be proportional to the concentration of the original solution, where the same volume of solution is introduced into the tube on each occasion. By contrast, for finely powdered samples, the relationship between initial sample weight, and the sample thickness, is less easily defined, unless the polymer melts and flows freely prior to the onset of decomposition.

In a study of the relationship between sample weight and degradation behaviour, care must be exercised to ensure that each sample is, as far as possible, introduced in the same physical form each time, since the sample form may have a profound influence upon the degradation behaviour.

Sample weight and Tmax.

The effect of initial sample weight on the position of Tmax was investigated for polystyrene NBS 706. The polymer was degraded as a film cast from a solution of the appropriate concentration in A.R. benzene. The range of sample size covered was 1 to 100 mg, the volume of solution used to introduce the polymer was 1 ml, and a heating rate of 10°/min. was employed. The result of this investigation is summarised in Table (3,2).

T A B L E (3,2).

Relationship between initial sample weight and the position of Tmax, for the degradation of Polystyrene NBS 706, at a heating rate of 10°/min. (Samples as films cast from 1 ml of appropriate solution in Analar benzene.)

Weight.	Tmax °C.	
	G_2	G_1
1	428	430
1	427	427
1	428	428
1	425	425
5	421	421
10	417	417
15	422	420
20	422	422
25	422	422
30	423	423
50	419	421
50	422	422
50	418	417
100	422	422
100	422	422

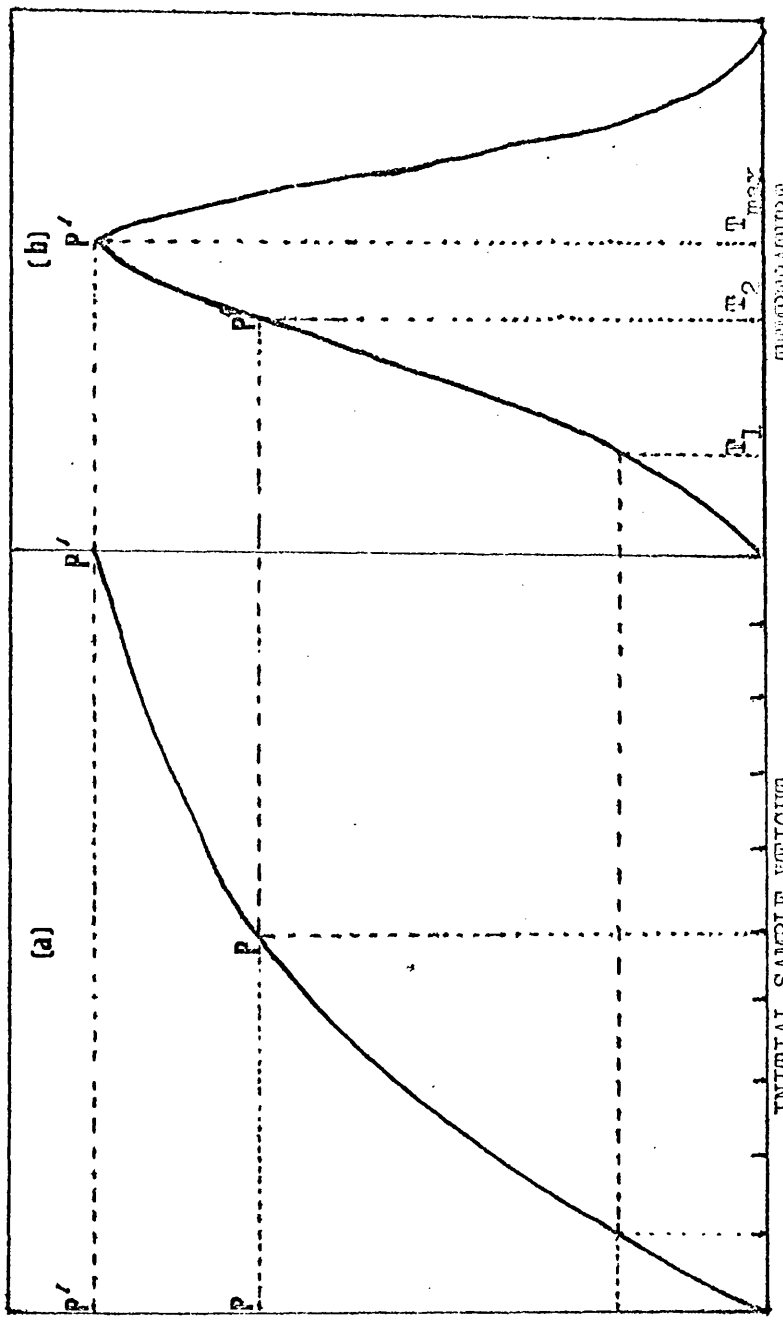
N.B. Assuming the density of polymer = 1, the thickness of a 1 mg. film = $1 \times 10^{-3}/10$

= 1×10^{-4} cm.

McNeill and Mohammed [67] have shown for films of polystyrene, where the weight is less than 1 mg, that the position of Tmax is displaced to higher temperatures (by up to 60° at a heating rate of 10°/min.). Some evidence of this phenomenon is to be seen in Table (3,2). The Tmax values for 1 mg samples are consistently above those for samples up to 100 mg. Clearly, however, the Tmax positions for samples above 1 mg are independent of initial sample weight or thickness. Indeed, in the absence of diffusion controlled volatilisation, it can be shown that the value of Tmax should be independent of initial sample weight.

Sample weight or thickness and rate of decomposition.

The Pirani output at any point on a TVA thermogram is a measure on a non linear scale of the absolute rate of volatilisation of a sample. This, in turn, is directly proportional to the initial weight of sample used, (i.e. doubling the initial sample weight doubles the rate of decomposition, providing the same conditions operate). However, the non linearity of the Pirani gauge means that doubling initial sample weight will not double the Pirani response (except where the response is below 1.0mV). A plot of Pirani output at a specified temperature, against initial sample weight would have the appearance shown in figure (3,9,a)

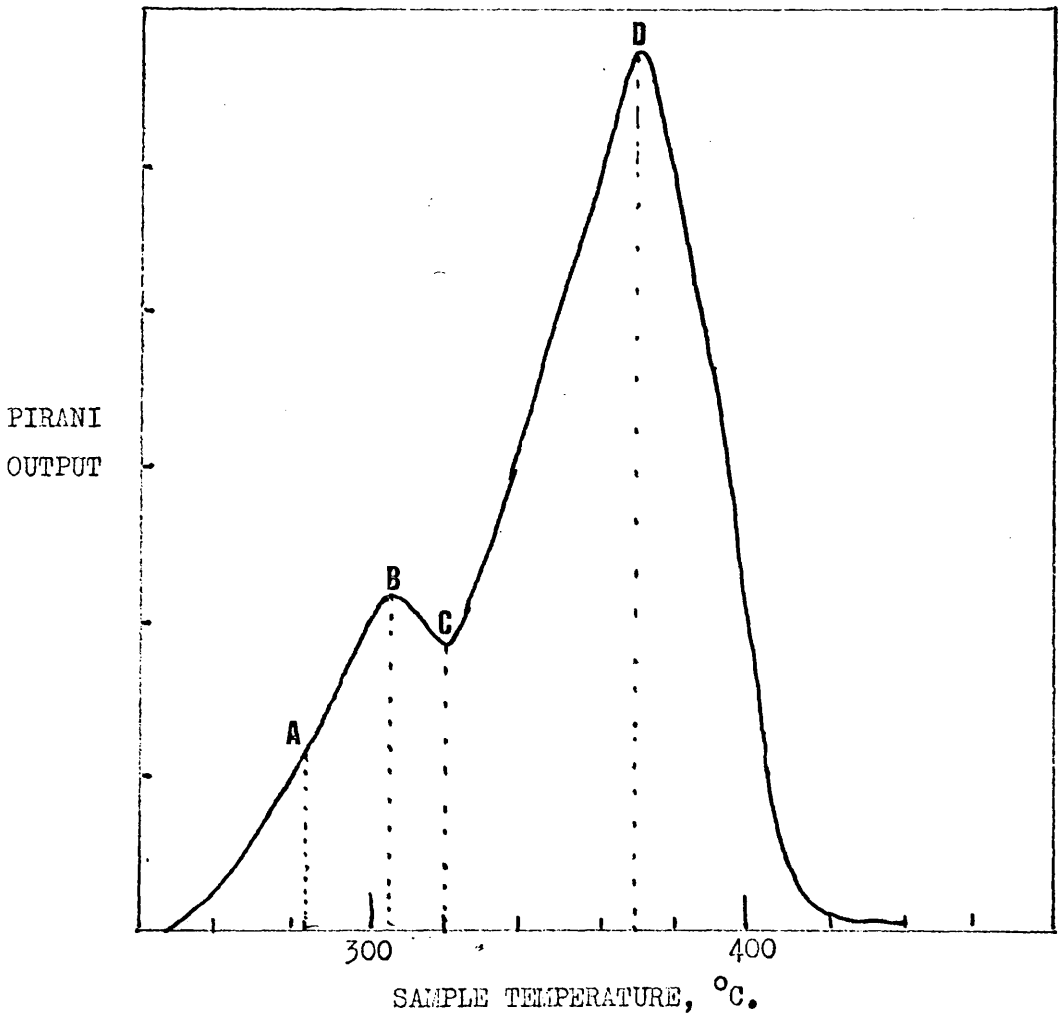


FIGURE(3,9),The Use of a Plot of Pirani Output Against Initial Sample Weight as a Relative Calibration Graph.

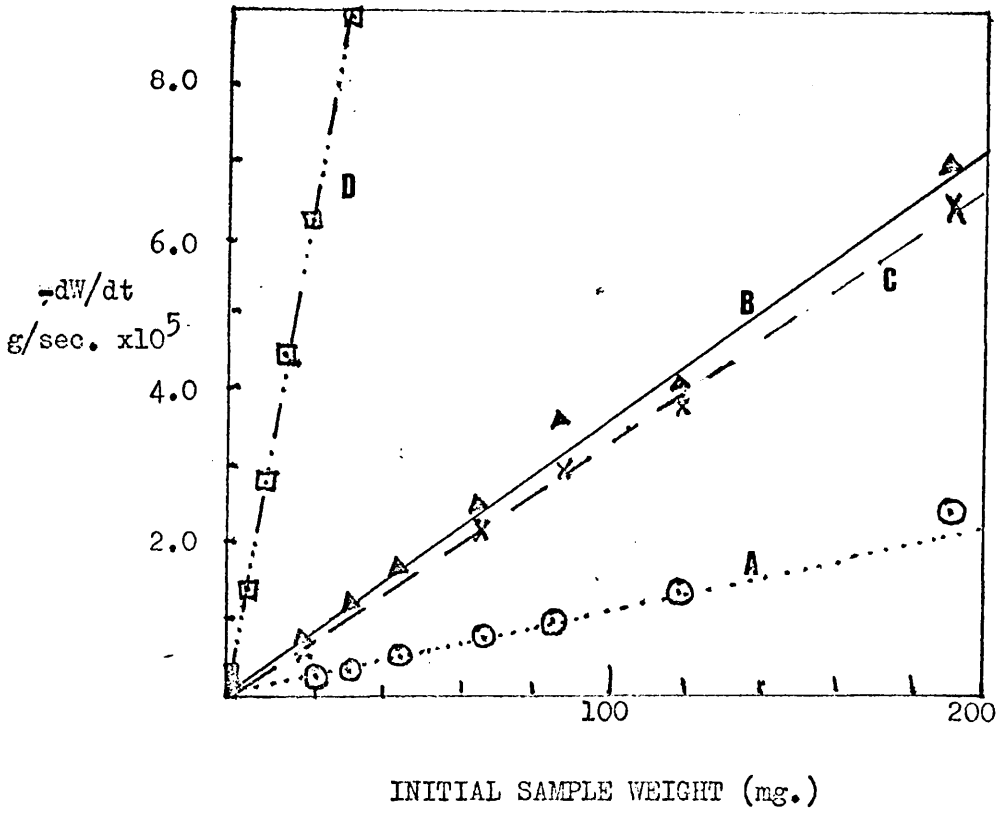
a shape similar to that of a calibration plot. (Such a plot, for degradation of natural rubber samples, has been obtained by McNeill and Millrine [68]).

However, where a calibration plot is available for the Pirani gauge, then it should be possible to relate Pirani output to rate of production of volatiles directly. This was done in the case of the decomposition of PMMA.DF (see Appendix I), utilising the calibration data for methyl methacrylate. Samples of various weights (cast as films from 1 ml portions of benzene solution) were degraded at 10°/min. A typical thermogram is shown in figure (3,10). For each initial sample weight, the rates of evolution of methyl·methacrylate were computed from the appropriate Pirani output, at points A, B, C, D on the thermogram. These rate values were then plotted against the appropriate initial sample weight as shown in figure (3,11). The plots are linear within experimental error.

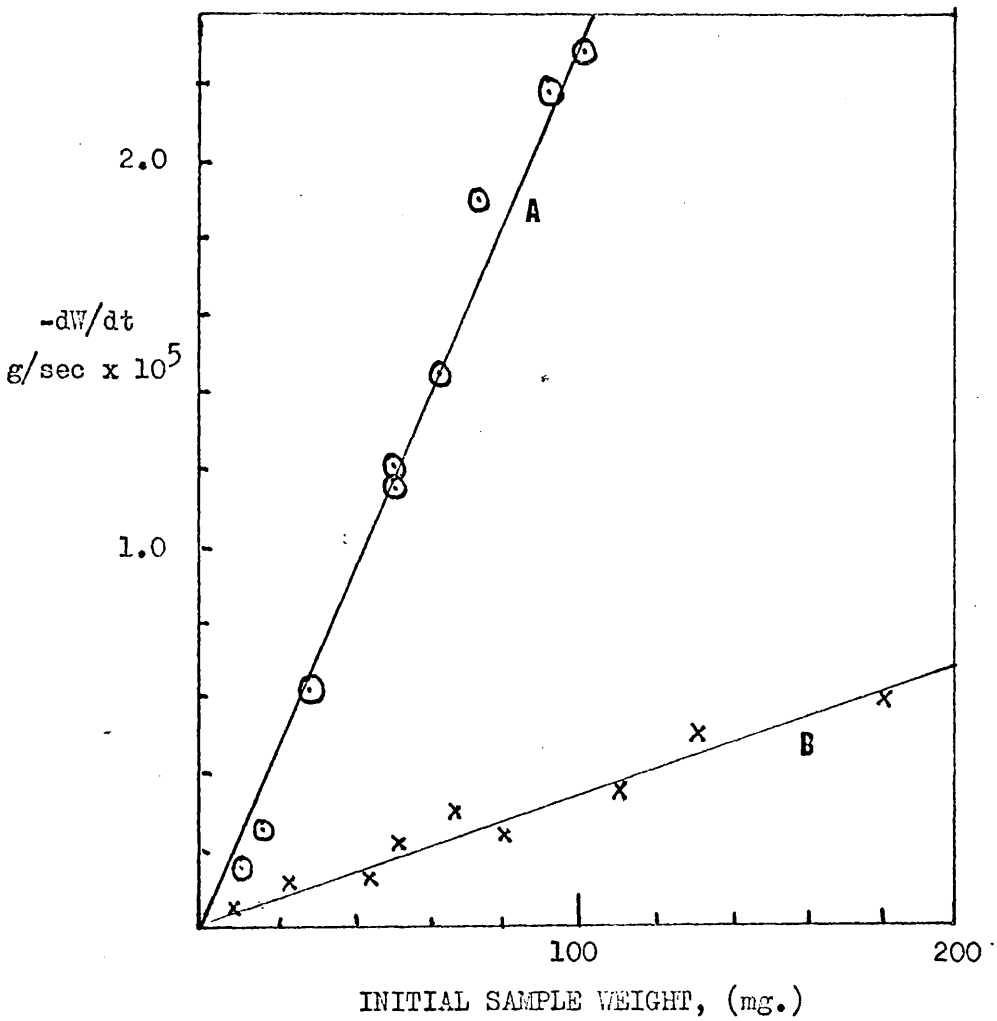
Graphs of initial sample weight against rate of degradation at 378°C were likewise obtained, using the styrene calibration data, for two samples of polystyrene, NBS 706, and PS. cat. The plots, shown in figure (3,12) suggest that PS. cat is more stable than NBS 706, presumably due to the different modes of preparation of the two polymers (see Appendix I).



FIGURE(3,10), Tva thermogram, at 10°/min., for the decomposition of PMMA DF.



FIGURE(3,11), Graph of rate of sample decomposition against initial sample weight, at the temperatures A,B,C, and D, (see figure(3,10)), for the decomposition of PMMA DF.



FIGURE(3,12), Graphs of rate of sample decomposition, at 378°C, for two samples of polystyrene heated at 10°/min., against initial sample weight

A=Polystyrene NBS 706, B=Polystyrene Cat.

In film samples, the sample thickness can be taken as being directly proportional to the initial sample weight. For example, taking the area of base of the degradation tube as 10 sq. cm., 100 mg of polymer has a mean film thickness of 10^6 Å.

A plot of film thickness against rate of degradation has been used by some workers as a test for diffusion controlled decomposition. For example, Barlow, Lehrle and Robb [69] using pyrolysis/glc, showed, by means of such a plot, that above a film thickness of 400 A, the rate of decomposition of poly (methyl methacrylate) was diffusion controlled, and depended on film thickness. The upper limit for polystyrene was similarly found to be 250 A.

The linearity of the plots in figures (3,11) and (3,12) suggest that in the TVA work diffusion controlled decomposition is absent, even in samples above 10^6 A thickness. Some explanation must be found to account for the different behaviour observed by these two techniques.

In pyrolysis/glc, the sample is subjected to a rapid pulse of energy in order that all the volatile products can be admitted simultaneously and in sufficient quantities to the injection port of the chromatography column. The temperature and the rate of sample decomposition are therefore made to increase rapidly.

In TVA, however, the temperature of the polymer is raised more gradually. It may be that in the latter case, the rates of decomposition and of escape of volatiles from the polymer environment, are more nearly comparable.

It is possible that the continuous evacuation of the sample which is present in TVA is capable of removing the products more efficiently from the decomposing polymer than the flow of carrier gas used to purge the sample in pyrolysis/glc. Another, more fundamental reason, may be that the mechanism of degradation of polymer is a function of sample thickness, as suggested by the results of Jones and Moyles [28], Knight [70] and McNeill and Mohammed [67].

Alternative calibration method.

A further point concerning the relationship between sample weight and rate of decomposition can be brought out at this stage.

Consider figure (3,9,a). This shows the Pirani output at a fixed temperature on a TVA thermogram, as a function of initial sample weight. In the absence of diffusion phenomena, it can be assumed that the rate of product evolution from the polymer is directly proportional to the initial sample weight. Thus the Pirani output P corresponds to half the rate of

decomposition implied by P', since the sample weights corresponding to these outputs are in the ratio 1 : 2.

A similar argument can be applied to the thermogram illustrated in figure (3,9,b). If the rate of decomposition at Tmax is r, then the rate at T_1 will be 0.1r, while at T_2 the relative rate will be 0.5r, and so on. In this way figure (3,9,a) can be used as calibration graph for the thermogram, making it possible to show how the rate of volatilisation is changing with temperature.

The following assumptions are made, however, in using this procedure:-

(1) No diffusion control is present.

(2) The volatile products do not change their relative proportions during the decomposition process.

Providing these conditions operate, the method may be useful where calibration data cannot be obtained from first principles.

SAMPLE FORM.

The effect of sample form on the TVA thermograms of PS cat and PMMA DF (see Appendix 1) was examined. In each case, equal weights (15 mg.) of the polymer were degraded, at 10°/min, in three different sample forms:-

(a) As a film, cast from 1 ml of a solution of the polymer in benzene.

(b) As a powder, obtained by freeze-drying a benzene solution of the polymer.

(c) As a fine powder, capable of passing through a 0.0049 in. mesh.

For each polymer, the Tmax and the Pirani output at Tmax were compared, over four runs for each sample form.

For PMMA DF, no detectable differences in Tmax were observed over the range of sample form in question.

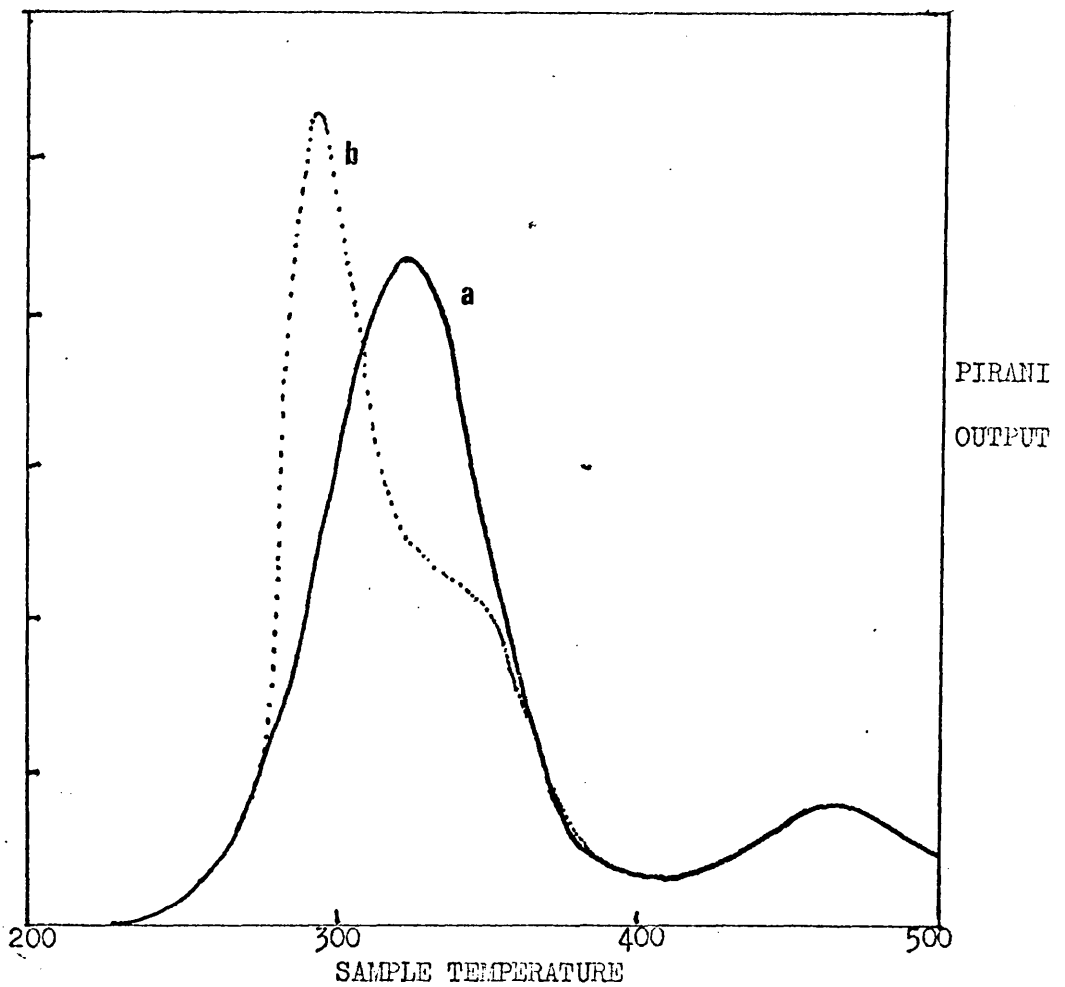
In the case of PS cat, very slight differences were observed:-

(i) Tmax values for film samples were consistently 3-4^{o} higher than for powdered samples.

(ii) Rate values at Tmax for film samples were marginally higher (by 2%) than for powdered samples.

Clearly, when precautions are taken to ensure that the sample is in a suitable form for degradation, sample form is not a crucial factor in determining the appearance of the TVA thermograms of these polymers.

In the case of the TVA thermograms of PVC samples, however, it has been found that sample form plays a much more serious role. This is illustrated in figure (3,13). The thermograms shown are for equal weights of the same PVC sample, degraded at a heating rate of 10^{o}/min (a) as a film cast from 1 ml of a cyclohexanone



FIGURE(3,13), Effect of Sample Form on the TVA Thermogram of PVC113 Samples of Equal Weights.

a, Sample as film cast from 1ml. of a cyclohexanone solution.

b, Sample as a fine powder.

(Both Thermograms at 10°/min.)

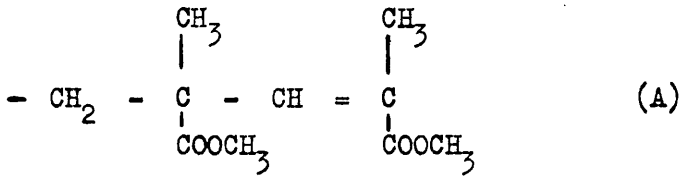
solution of the polymer, and (b) as a fine powder. Clearly a "shoulder" is present on the thermogram for the powdered sample, when compared with that obtained using a film sample. The different shapes of the two thermograms obtained cannot be easily explained. The powdered sample is presumably subject to diffusion controlled loss of hydrogen chloride, while the decomposition of film samples is less complex. The unusual shape of the thermogram of the powdered sample in particular, the rapid attainment of Tmax, may also be due in some part to the catalytic effect of entrained hydrogen chloride on the dehydrochlorination [71].

Obviously, when studying the TVA behaviour of any polymer system, it is essential to examine closely the effect of sample form on the thermogram, and for initial studies at least, the sample form which gives the simplest thermogram should be the one chosen for subsequent examination.

SAMPLE HISTORY.

In interpreting a TVA thermogram, attention must be paid to the origin or history of the sample under study. In the case of poly (methyl methacrylate) for example, McNeill [6] has shown that the TVA thermogram is strongly influenced by the catalyst system used to prepare the polymer, and the molecular weight of the final product. Samples prepared by a free radical mechanism

exhibit two degradation peaks, the first of which is believed to be due to depolymerisation to monomer, initiated exclusively at unsaturated end structures, probably of type (A) [72], formed in the termination step of free radical polymerisation:-



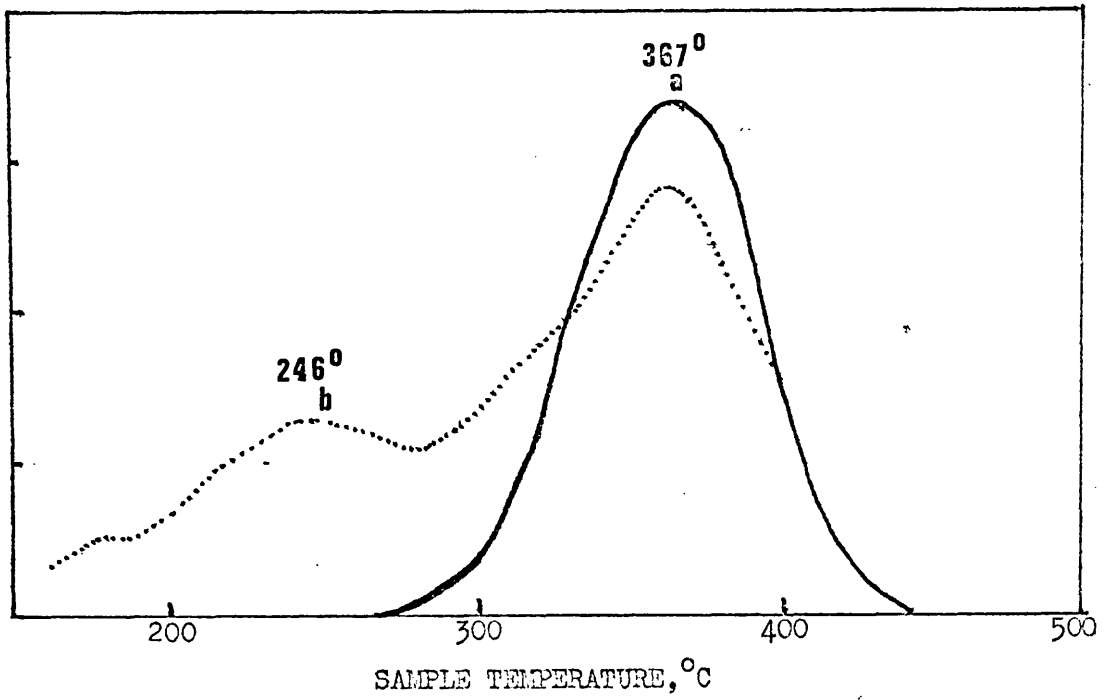
(A)

By contrast, the TVA thermogram of samples prepared using amonic catalysts, consists of only one peak (corresponding to the second peak of free radical samples), believed to be due to depolymerisation initiated by random scission of the main backbone. Unsaturated structures are not formed in amonic polymerisation.

When an amonically prepared polymer is exposed to ultra violet radiation, and a TVA thermogram is run of the irradiated polymer, new peaks appear on the TVA thermogram, as shown in figure (3,14). The earliest stages of breakdown of the pre-irradiated polymer are presumably due to degradation initiated at labile structures produced by the irradiation. It is apparent that these structures are significantly less stable than the end groups present in polymer prepared by free radical catalysts(see figure 3,10 and reference 6).

The action of UV light on poly (methyl methacrylate) has not

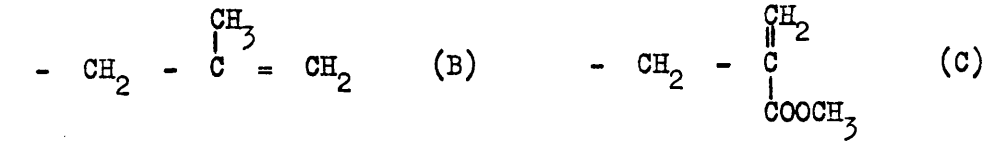
FIGURE(3,14), The Effect of Irradiation on the Thermal Stability of a Poly(methyl methacrylate) Sample.



a, Thermogram of PMMA anionic, before irradiation. (10°/min.)
b, Thermogram of the same weight of polymer, after U.V. irradiation. (U.V. irradiations carried out using Hg2537 radiation, with polymer as a film, at room temperature, under continuous evacuation.)

been fully elucidated. However, it hs been established [73] that at room temperature, the polymer undergoes a fall in molecular weight, concomitant with the evolution of small molecules, such as carbon monoxide, carbon dioxide, methane, and methyl formate, presumably arising from homolysis of the ester linkage. The appearance of a new band at 285 mμ in the ultraviolet spectrum of the photolysed polymer has also been noted, and has been ascribed to the production of conjugated unsaturation in the polymer chain. After long exposure to UV light, the infrared spectrum of the polymer also changes, and new bands at 1615 and 1640 cm^{-1} have been ascribed to olefinic linkages, produced in the polymer by irradiation. It has not been established, however, whether the production of unsaturation accompanies, or is a separate process from the chain scission reaction.

It has been suggested, however, that the chain scission reaction is accompanied by the formation of unsaturated end groups, of types B and C [74]:-



(B) (C)

By analogy with free radically prepared samples of poly(methyl (methacrylate), these structures might be expected to be labile

centres, at which depolymerisation could be initiated, and could therefore be responsible for the additional peaks in the TVA thermogram of irradiated polymer. However, it may be that UV irradiation is capable of producing unsaturation in the polymer backbone, rather than exclusively at chain ends. McNeill has shown, by study of the TVA thermogram of copolymers of phenylacetylene and methyl methacrylate [6], that unsaturation in the main chain of poly (methyl methacrylate) is also a source of instability.

Clearly, the origin of the photolytically induced TVA peaks is a problem requiring further examination.

Of the polymers so far studied by TVA, poly (methyl methacrylate) certainly appears to be the most sensitive to minute structural differences. However, McNeill and Mohammed [67] have shown that the TVA thermogram for polystyrene samples is somewhat dependent upon the molecular weight and mode of preparation of the polymer. Features of this kind, when carefully interpreted, can yield considerable information about the mechanism of degradation of the polymer. Where possible, therefore, the effect of molecular weight, and mode of preparation on the thermogram, should be an integral part of any study.

KINETIC PARAMETERS.

Kinetic Equation of a TVA Thermogram.

In a TVA thermogram, as in TGA, the sample is subjected to a linear rate of temperature rise, B, such that $B = dT/dt$, where T = sample temperature in degrees Kelvin, and t = time. The sample loses weight, the volatile fraction of the weight loss being detected by the Pirani gauge. The response of the Pirani gauge is a function of the absolute rate of weight loss of the sample, $- dW/dt$, where W = the residual reactive weight of the sample. If W_i is the initial weight of sample before decomposition, and W_f the residual weight after weight loss has terminated, we can define W_o, the initial reactive weight as $W_o = (W_i - W_f)$.

In deriving a theoretical TVA thermogram, we wish to describe quantitatively the relationship between Pirani output and temperature, for a known value of B. Since Pirani output can be related, by a suitable calibration graph, to $- dW/dt$, we will seek to describe the variation of the latter with temperature, which will permit the application of the well known treatments of the problem for DTG [38].

We shall assume that the process leading to weight loss has a rate constant k, which varies with temperature T according to the Arrhenius relationship, $k = A \exp(- E/RT)$, and that this relationship holds during a temperature programmed experiment.

(A and E are the "pre exponential" factor and energy of activation respectively, while R = gas constant, 1.987 cals degree^{-1} mole^{-1}).

By analogy with a TGA thermogram, we have

$$- 1/W_o \, (dW/dt) = k \, (W/W_o)^n \qquad (1)$$

where n is the "order" of the reaction.

If n is 1, we have

$$- 1/W_o \, (dW/dt) = A \, (W/W_o) \exp (-E/RT) \qquad (2)$$

$$\text{i.e. } - dW/W = A \exp (-E/RT) \, dt. \qquad (3)$$

$$\text{Now } dT/dt = B \qquad (4)$$

$$\text{Thus } - dW/W = (A/B) \exp (-E/RT) \, dT. \qquad (5)$$

When the reaction attains the temperature T, the initial weight W_o changes to W, thus

$$- \int_{W_o}^{W} (dW/W) = (A/B) \int_{0}^{T} \exp (-E/RT) \, dT. \qquad (6)$$

$$\text{i.e. } \ln W_o - \ln W = AQ/B \qquad (7)$$

$$\text{where } Q = \int_{0}^{T} \exp (-E/RT) \, dT.$$

$$\text{Thus } W = W_o \exp (-AQ/B) \qquad (8)$$

Substituting (8) in (2), we have:

$$- dW/dt = AW_o \exp (-E/RT - AQ/B) \qquad (9)$$

Which is the equation of a differential weight loss curve for a reaction order of one.

Where n is not 1 we have

$$- dW/dt = AW_o (1 - AQ (1-n) /B)^{n/1-n} exp (-E/RT) \qquad (10)$$

At this stage the following points should be made:-

(a) In deriving equations (9) and (10) it has been assumed that a single rate constant k, can be used to describe the reaction. This may not be the case for a polymer decomposition.

(b) In equation (10), n may have little or no direct significance as regards the mechanism of the weight loss process. Rather it is a curve-fitting parameter [38].

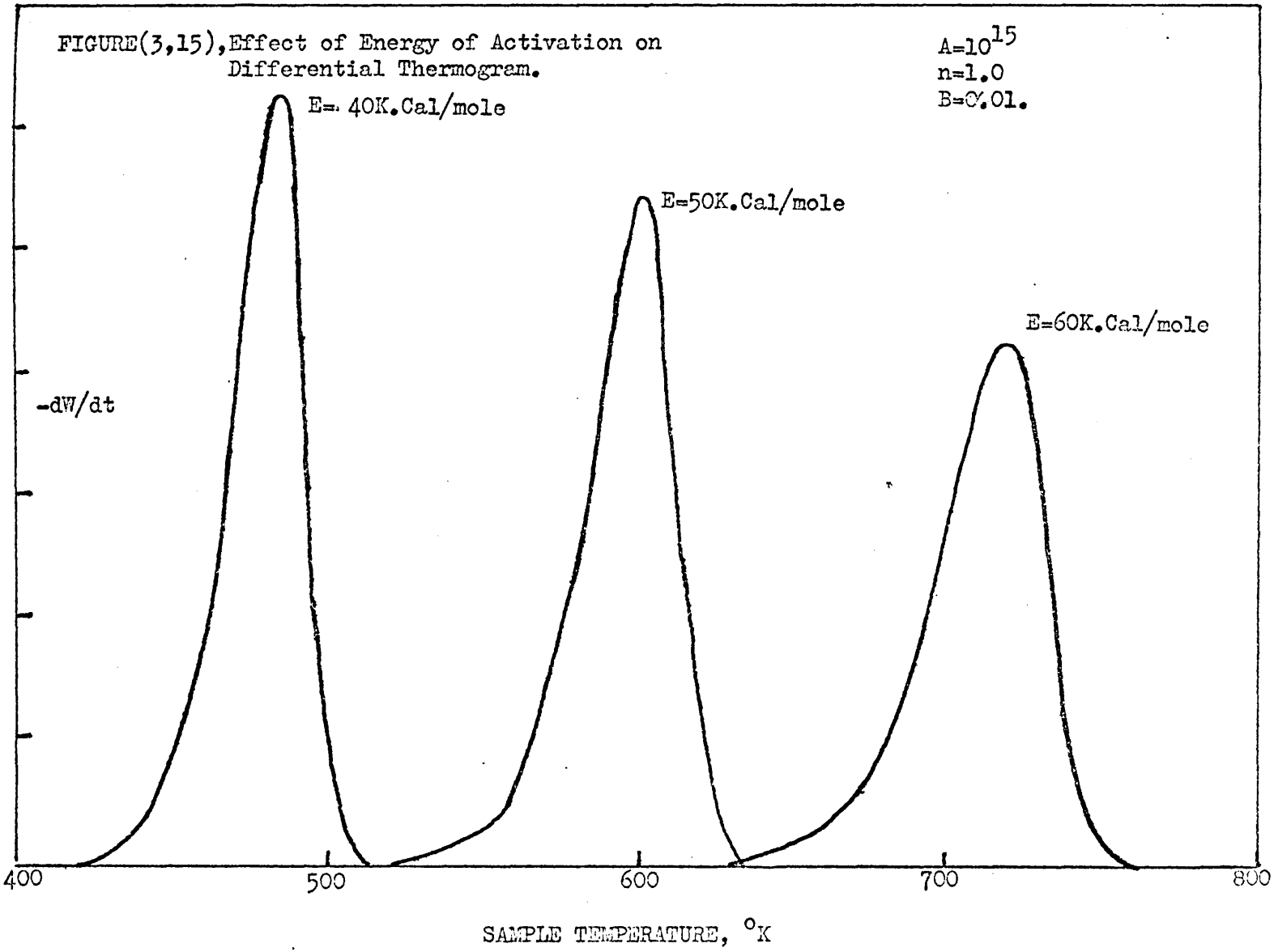
(c) It has been assumed that a linear rate of heating B, applies throughout the decomposition. Unless this is so, the equation is not applicable.

(d) The approximation can be made for Q, which is within an error of 1%, namely $Q = (RT^2/E) \exp (-E/RT)$ [75].

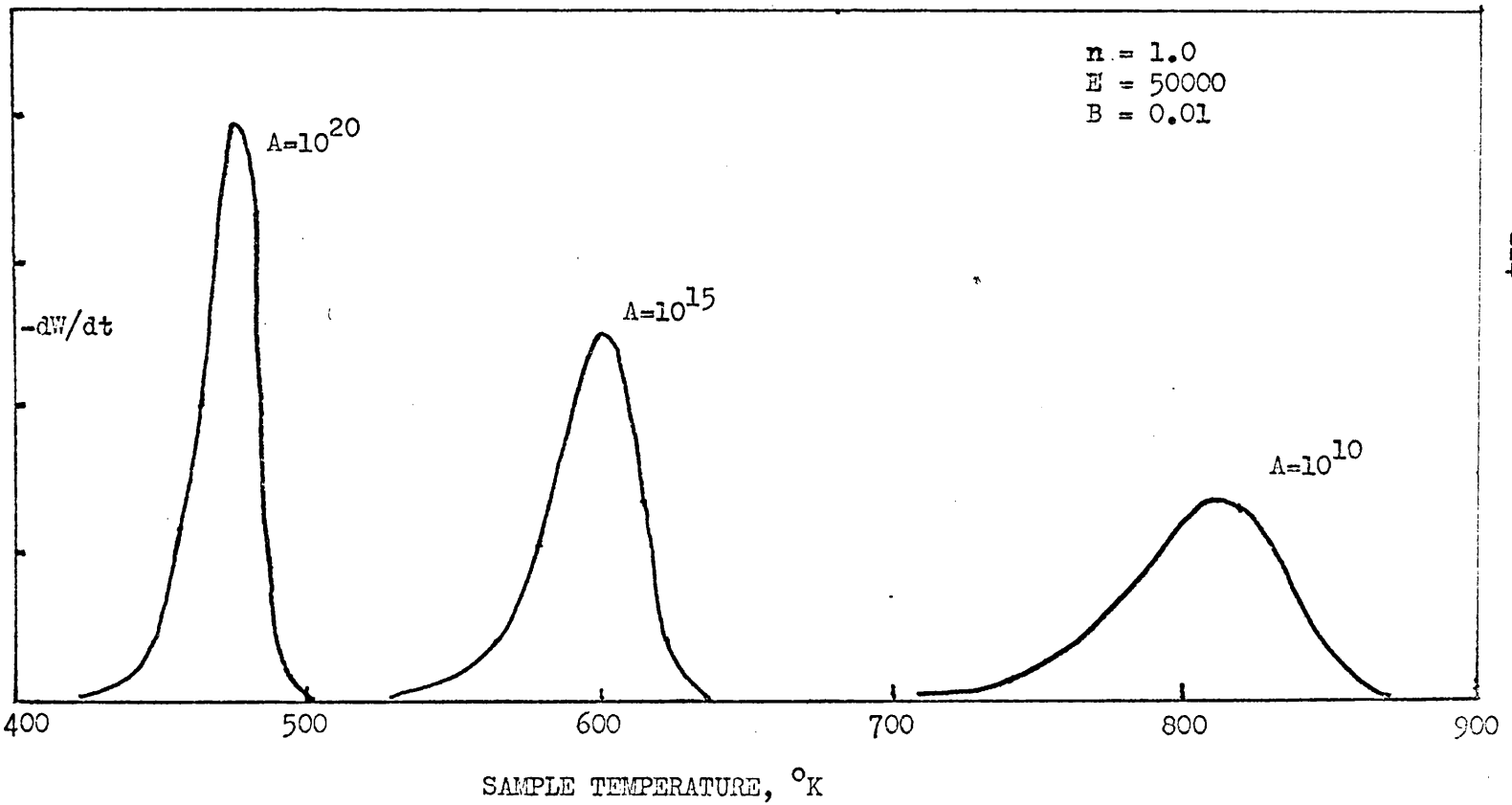
It is of interest to follow the effect of varying the various parameters A, E, n, etc. upon the resulting thermogram. The necessary calculations being somewhat tedious, a computer programme was written to perform them. (see Appendix 11).

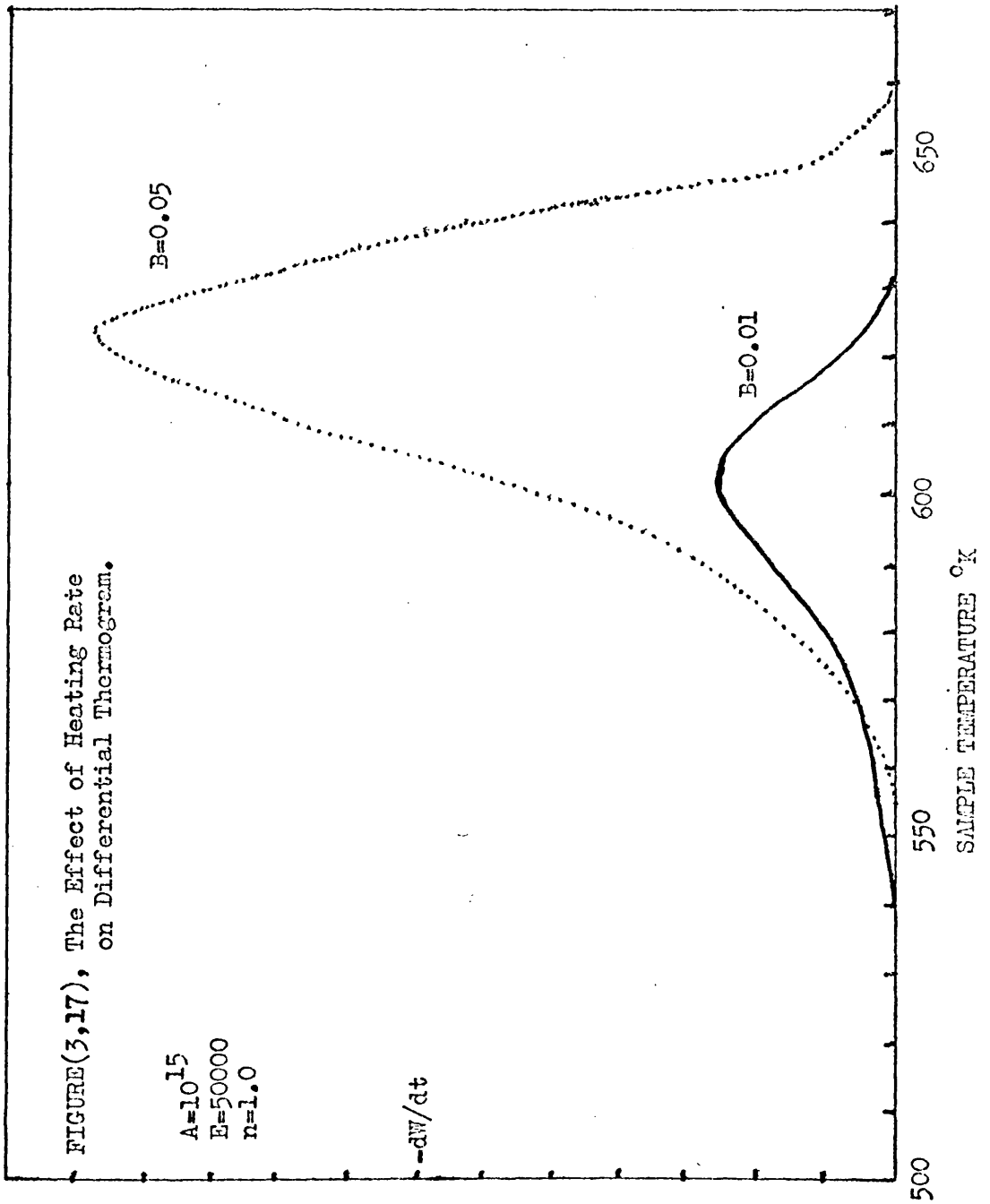
The results of this work are summarised in figures (3,15) to (3,18).

The TVA thermograms plotted in figure (3,15) are reminiscent in shape of the polystyrene thermogram, or other simple single peak thermogram.


FIGURE(3,15),Effect of Energy of Activation on Differential Thermogram.
A=10^15
n=1.0
B=0.01.
E=40K.Cal/mole
E=50K.Cal/mole
E=60K.Cal/mole
-dW/dt
400
500
600
700
800
SAMPLE TEMPERATURE, °K

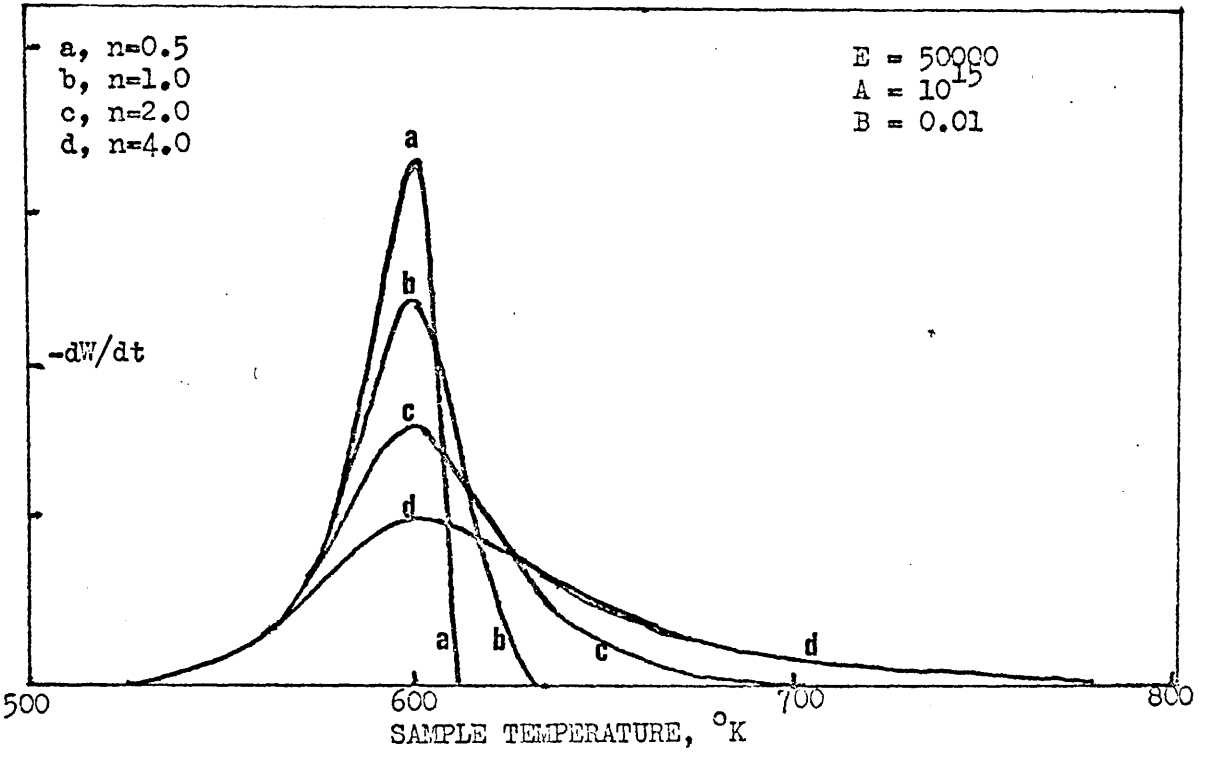
FIGURE(3,16), The Effect of Pre-Exponential Factor on Differential Thermogram.





FIGURE(3,17), The Effect of Heating Rate on Differential Thermogram.

FIGURE(3,18), The Effect of Reaction Order on Differential Thermogram.



It is evident that reactions of higher energy of activation tend to give decomposition peaks at higher temperatures, figure (3,15). Peak broadening and a consequent reduction in the maximum rate of weight loss also occurs. The area under each curve remains constant for the same initial sample weight, however. A decrease in A factor clearly has a similar effect to an increase in E, (see figure (3,16).

The predicted effect of heating rate is identical to that observed in the thermogram for NBS 706, (compare figure (3,8) and figure (3,17), confirming that peak positions are influenced by the rate of temperature rise.

The position of Tmax is not altered markedly by changing the exponent n, (see figure (3,18), although the thermogram shape is clearly changed. In particular for orders less than 1, the weight loss is complete shortly after the attainment of maximum rate. For orders above unity, a significant proportion of weight loss occurs after the Tmax is attained.

In short, this series of plots serves to show that shape and position of a TVA thermogram is a complex function of the kinetic parameters of the process involved. It is therefore impossible to tell by inspection of the TVA thermogram what are the kinetic parameters of the reaction.

CONCLUSIONS.

It is appropriate at this point to review the points discussed in this chapter.

The Nature of Pirani Response.

The response of a Pirani gauge in a TVA system, to a given flow rate of material depends upon:-

(a) The nature of the substance or substances passing the filament.

(b) The position of the gauge head relative to the heated sample and the cold trap.

A pressure gradient is present between the heated sample and the cold trap when condensable products are produced, and between the sample and the pumping system when the products are not condensed by the trap. For condensable products, the main "pumping force" is the cold trap, the pumps playing only a secondary role.

The Differential Character of a TVA Thermogram.

The response of the Pirani gauge at any time or temperature is a measurement, on a non linear scale, of the rate of volatilisation of the sample under study. It is possible to obtain an estimate of the absolute rate of formation of a given product (i) when it is the only product formed, or (ii) when that product can be isolated from the main product stream by selective

condensation or adsorption of the other products formed. In any case it is necessary to calibrate the gauge head at known rates of transfer of the substance under the same conditions as exist during degradation.

The Pirani calibration data presented in this chapter and also that for HCl [76] and isobutene [77] suggest that the Pirani output is approximately linear with flow rate up to 2 mV. In this range, therefore, Pirani output gives a measure of the relative rate of decomposition on a linear scale. Thus if the sample weight of the polymer is adjusted so that the maximum response lies below 2 mV, the Pirani output at any point can be taken as a direct measure of the rate of volatilisation.

Alternatively, where a significant part of the thermogram lies in the non linear region of Pirani response, a plot of the Pirani output at a particular temperature, against the initial sample weight, can be made to serve as a calibration graph from which the relative rates of volatilisation at various temperatures can be deduced.

Thus various methods exist whereby a TVA thermogram can be converted to a differential rate plot for the decomposition.

Interpretation of a TVA Thermogram.

It is possible that a single TVA peak may represent more

than one process. Such concurrent processes might have independent mechanisms. The differential condensation technique, by separating the products before they are detected by the gauge head, may help towards resolving the various reactions, giving a TVA thermogram a "fine structure" which is not apparent when the thermogram is obtained on a conventional system.

The position of a thermogram on the temperature scale is difficult to define in quantitative terms. The temperatures Ti and Tf, as defined in figure (3,1) will depend upon the heating rate employed, the weight of sample used, and the Pirani sensitivity, in addition to the fundamental kinetic parameters A, E and n for the process.

For a given heating rate, the Tmax position is almost independent of the reaction order n, being a function of the A and E parameters for the process. For diffusion-free processes, however, Tmax is independent of the initial sample weight.

By contrast, the height, H, of a TVA peak is a function of initial weight of sample used, and increases for increasing heating rate. For the same weight of sample, an increase in n or A, causes the value of H to rise. An increase in the value of E causes the peak height to fall, with a consequent broadening of the thermogram.

Many thermograms consist of more than one peak, and the

number of peaks can be taken as an indication of the number of separate stages in the decomposition of the substance. However, "shoulders" on main peaks may be due to sample form effects, and must be investigated closely in this context.

In a complex thermogram (i.e. more than one peak), the Tmax position of each peak may be a function of the "overlap" of the various reactions. Again, the differential condensation method may help to resolve the various peaks.

Limitation of TVA.

It has been pointed out that only those processes which give rise to substances which are sufficiently volatile to reach the Pirani filament will be recorded in a TVA thermogram. This means that not all the processes detected by thermogravimetry can be detected by TVA. In this respect, TVA is similar to other gas evolution analysis methods, such as MTA or pyrolysis/glc.

However, the great sensitivity of the Pirani gauge means that even when only a small proportion of the weight loss of a sample is due to products which are volatile at room temperature, a TVA thermogram can be obtained. Thus polyethylene, which gives less than 5% volatile material during decomposition, has a characteristic thermogram [66].

Advantage of TVA.

As discussed in Chapter 2, the method of sample preparation used in TVA means that temperature gradients within the sample are minimised, and sample temperature can be accurately measured.

Furthermore, the large area available for the sample, and the continuous and efficient removal of the products from the reaction zone, are factors which tend to reduce the chances of diffusion controlled processes occurring in TVA. Considerable care must still be exercised to ensure that the thermogram is not dependant on sample form. For initial studies at least, that sample form which gives the simplest thermogram should be adopted for subsequent investigations.

CHAPTER FOUR.

KINETIC DATA FROM TVA.

Any worker in the field of Thermal Analysis will agree that a major preoccupation in much of the literature has been to devise methods of obtaining meaningful quantitative information from thermograms obtained under non-isothermal conditions. This is particularly true of thermogravimetry where several methods have been devised for obtaining values of E, A and n for the decomposition process under study. These methods have been recently collated and criticised by Flynn and Wall [38] and by Doyle [103].

In Chapter Three it was established that a TVA thermogram and a DTG thermogram could to a first approximation, be regarded as equivalent. It might be thought, therefore, that any method of determining kinetic parameters from DTG traces would be applicable to TVA thermograms.

Unfortunately, the situation is complicated in TVA by the non-linearity of the Pirani response, and the different response which the gauge head has towards the same pressure of different substances. Furthermore, in many cases, decomposing polymers evolve a mixture of products e.g. monomer, dimer, trimer, each

component of which will add to the overall Pirani output, unless the more condensable substances can be removed from the product stream by selective condensation.

In any study of reaction kinetics by TVA, one of two alternative approaches must therefore be adopted. Either a method must be devised by determining useful kinetic parameters without requiring prior calibration of the Pirani gauge, or the gauge head must be calibrated for the substance concerned, in the manner described in Chapter Three (pages 69-72).

In this Chapter, some of the methods which have been used in this work to determine kinetic parameters will be discussed, and some experimental results presented. It is not intended to imply that the methods described are the best or the only methods which can be used, but rather that it <u>is</u> possible to determine kinetic parameters using TVA.

<u>Activation Energy Without Pirani Calibration</u>.

TVA thermograms, like thermograms obtained from any differential technique (DTG, DTA, DSC, MTA), have the characteristic feature of passing through a "maximum". Study of figures (3,15) to (3,18) show that the position of Tmax is a function of heating rate (B), energy of activation (E), pre-exponential factor (A), although to all intents and purposes, is independent

of the reaction "order", n.

The condition that the TVA thermogram should pass through a maximum is, for n = 1,

$$d/dT\ (AW_o \exp\ (-E/RT - AQ/B)\ ) = 0 \qquad (4,a)$$

where $Q = \int_0^T \exp\ (-E/RT\ )dT$

similarly, where n≠1, we have

$$d/dT\ \{AW_o\ (1 - AQ\ (1-n)\ /B)^{n/1-n} \exp\ (-E/RT)\ ) = 0 \qquad (4,b)$$

It follows from (4,a) that the TVA thermogram for a first order reaction passes through a maximum, if and only if:-

$$E/RT^2_{max} = (A/B) \exp\ (-E/RT_{max}) \qquad (4,c)$$

i.e. $$\log B - 2 \log Tmax = (-E/2.303RT_{max}) - \log (E/RA) \qquad (4,d)$$

Thus a plot of log B - 2 log Tmax against 1/Tmax should be a straight line whose slope is - E/2.303R.

Such an equation has been derived by Kissinger [104] who has also shown that a similar relationship holds approximately where n ≠ 1, which is not unexpected, in view of the small effect which changing n has upon the position of Tmax (see figure (3,18)).

The use of this, and other methods of obtaining kinetic parameters from TVA thermograms, utilising the observed Tmax value, has been suggested by Cameron and Fortune [105]. Of the

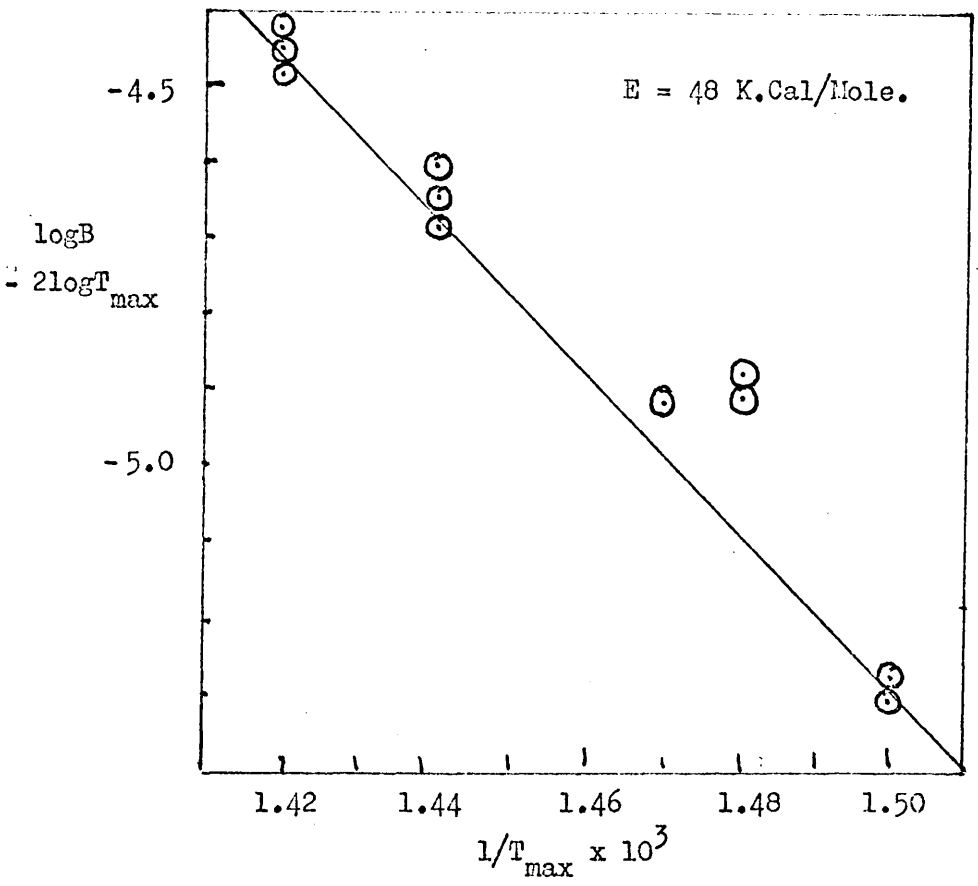
methods proposed by these authors, that utilising equation (4,c) is the only one which does not require prior Pirani calibration.

Equation 4 (d) was used to derive energy of activation values for polystyrene (NBS 706), poly (methyl methacrylate) (I.C) and poly (vinyl chloride) (PVC 113). In the case of the last named polymer, the E value obtained for powdered samples was compared with that obtained for film samples.

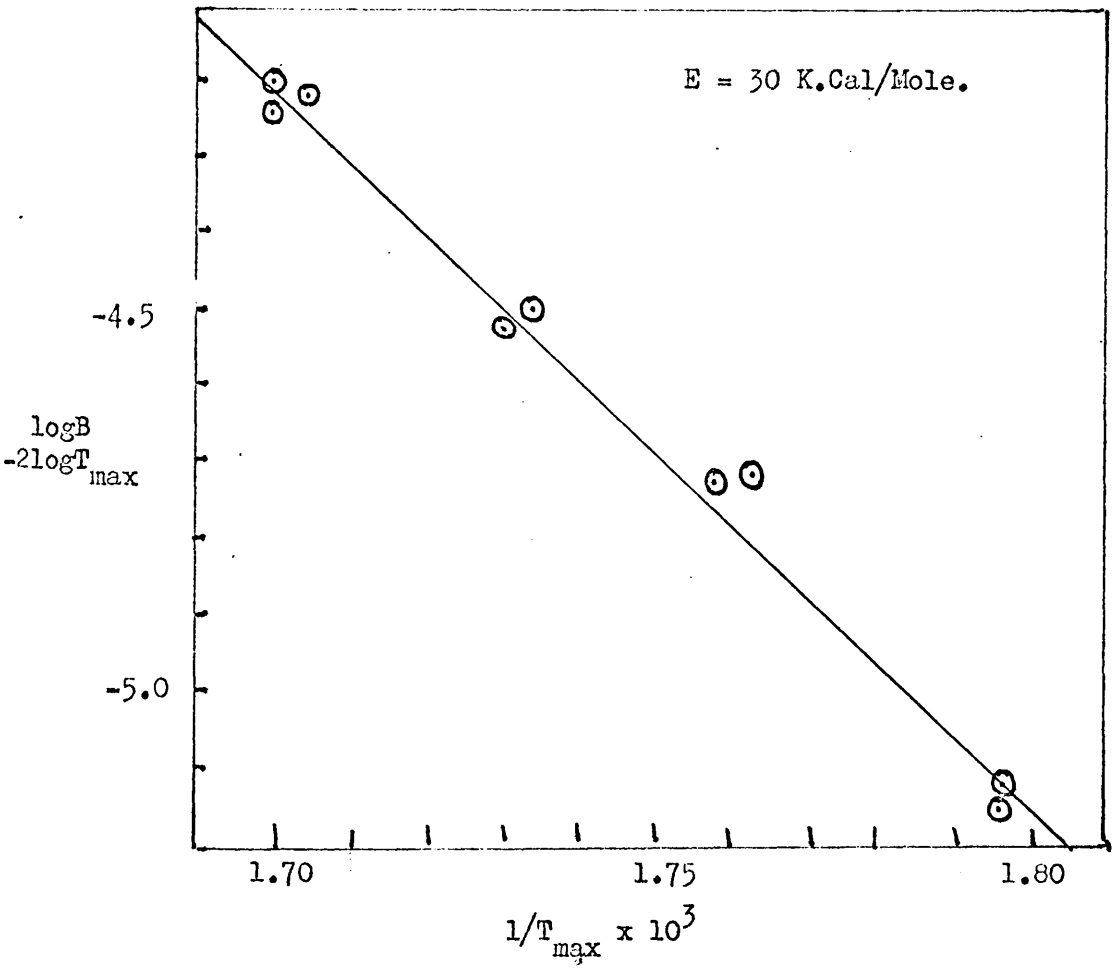
The appropriate graphs are shown in figures (4,1) to (4,5).

In the case of polystyrene, the value of E determined by this method (48 K Cal/mole) is lower than the value quoted by Madorsky[106] (58 K Cal) for this polymer. The value quoted by Jellinek [107] is 45 K Cal, while the results of Anderson and Freeman [108] suggest that at low extents of degradation, E=46 K Cal, rising to 60 K Cal/mole at higher extents of conversion. Clearly it would be of interest to examine the effect of molecular weight, and mode of preparation, on the E value for this polymer.

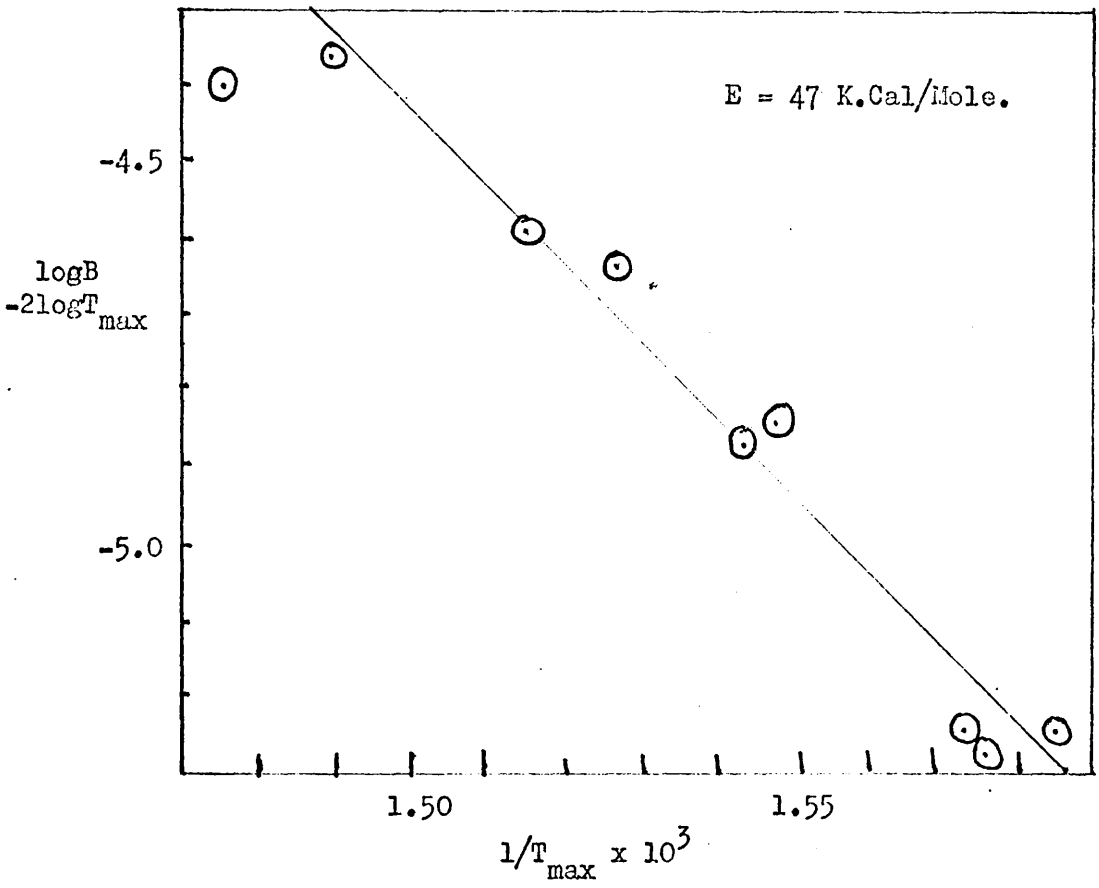
In the case of PMMA I.C., two graphs are shown, corresponding to the two peaks in the TVA thermogram. As might be expected, the E value for the lower temperature peak (depolymerisation initiated at chain ends) is less than that for the upper temperature peak (depolymerisation initiated by random, main chain scission). Too much significance should not be placed upon the absolute values



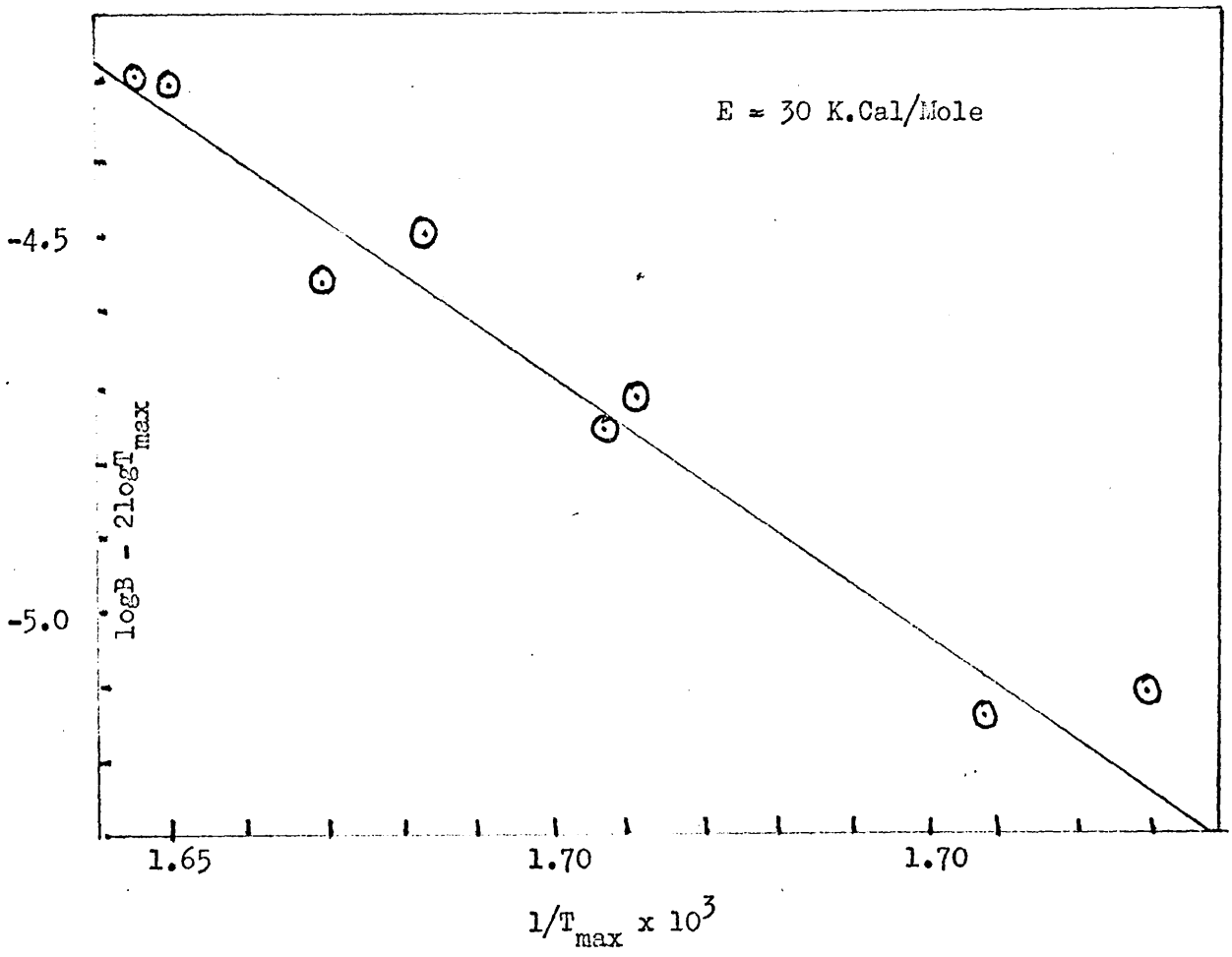
FIGURE(4,1), Application of the Kissinger method of determining Energy of Activation for polystyrene NBS 706.



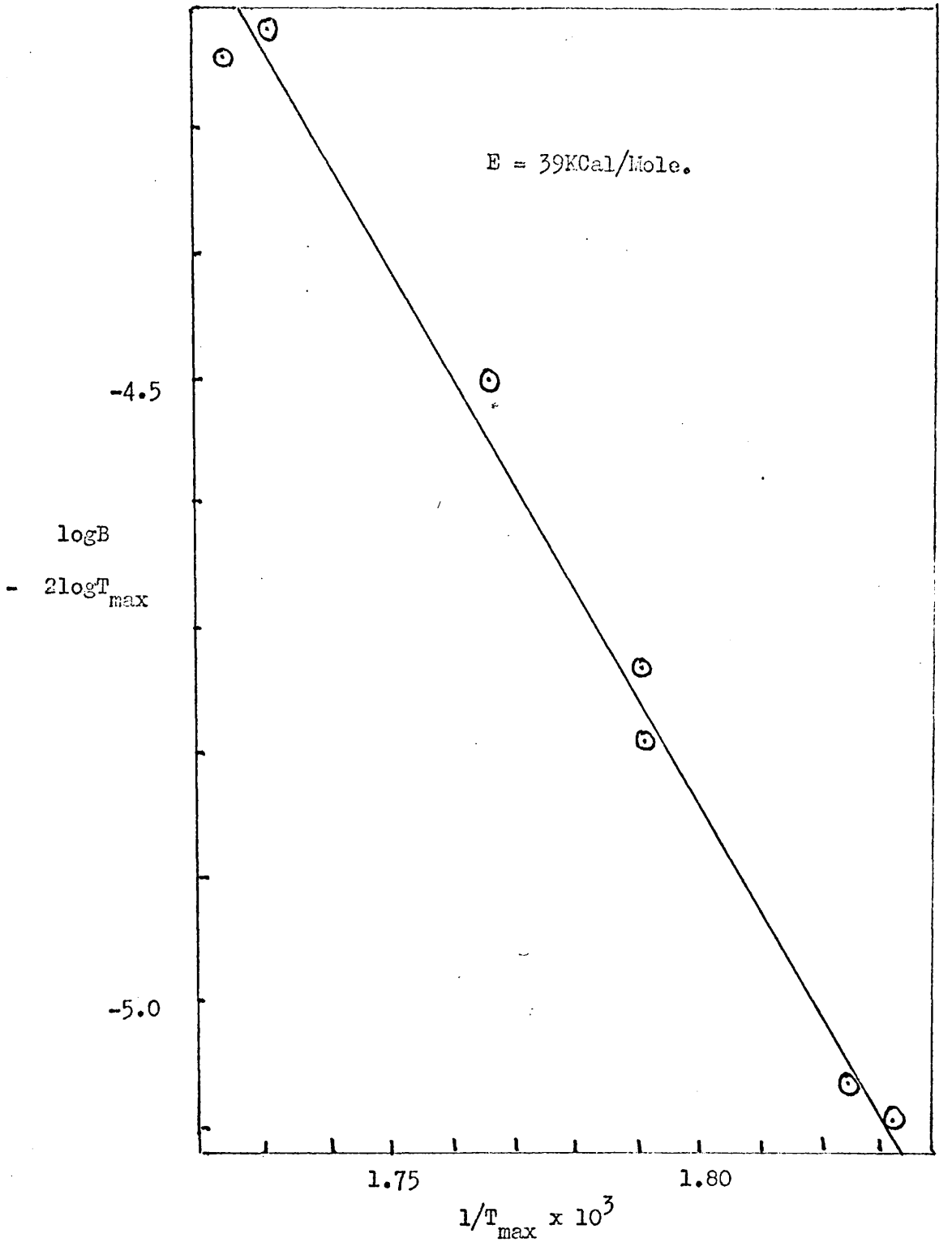
FIGURE(4,2), Application of the Kissinger method of determining Energy of Activation for PMMA I.C. (for low temperature, chain end initiated decomposition)



FIGURE(4,3), Application of the Kissinger method of determining Energy of Activation for the decomposition of PMMA I.C., (upper temperature, random initiated, depolymerisation)



FIGURE(4,4), Application of the Kissinger method to determine the Energy of Activation for the dehydrochlorination of PVC 113, sample as a film, cast from cyclohexanone.



FIGURE(4,5), Application of the Kissinger method to the dehydrochlorination of powder samples of PVC 113

obtained by this method, since the peaks overlap considerably in the thermogram, so that a contribution from the high temperature decomposition reaction will inevitably be imposed on the lower temperature peak, and vice versa. It has also been shown that the energy of activation for the decomposition of this polymer is a function of temperature, molecular weight, and extent of degradation[109].

The E value obtained by this method for the dehydrochlorination of PVC film samples (30 K Cal) falls within the range of values (26 - 32 K Cal/mole) observed by Stromberg [13]. It was found that for powdered samples of this polymer, the E value obtained by this method was 39 K Cal/mole. Presumably in the latter case, diffusion effects cause this increased value.

The use of Pirani Calibration.

(a) Initial Rates.

Consider the equation for a TVA thermogram

$$-(1/Wo)dW/dt = A\,(W/Wo)^{n}\exp(-E/RT) \qquad (4,e)$$

We have $\log(-dW/dt) = \log A + n\log W + (1-n)\log Wo - E/2.303RT$ (4,f)

In the early stages of a decomposition reaction, weight loss is small so that in a small temperature change dT, it can be assumed that W is almost unchanged, because of the small rates

of decomposition which operate.

We can thus assume that, providing weight loss is small, we have

$$\log(-dW/dt) = \text{constant} - E/2.303RT. \qquad (4,g)$$

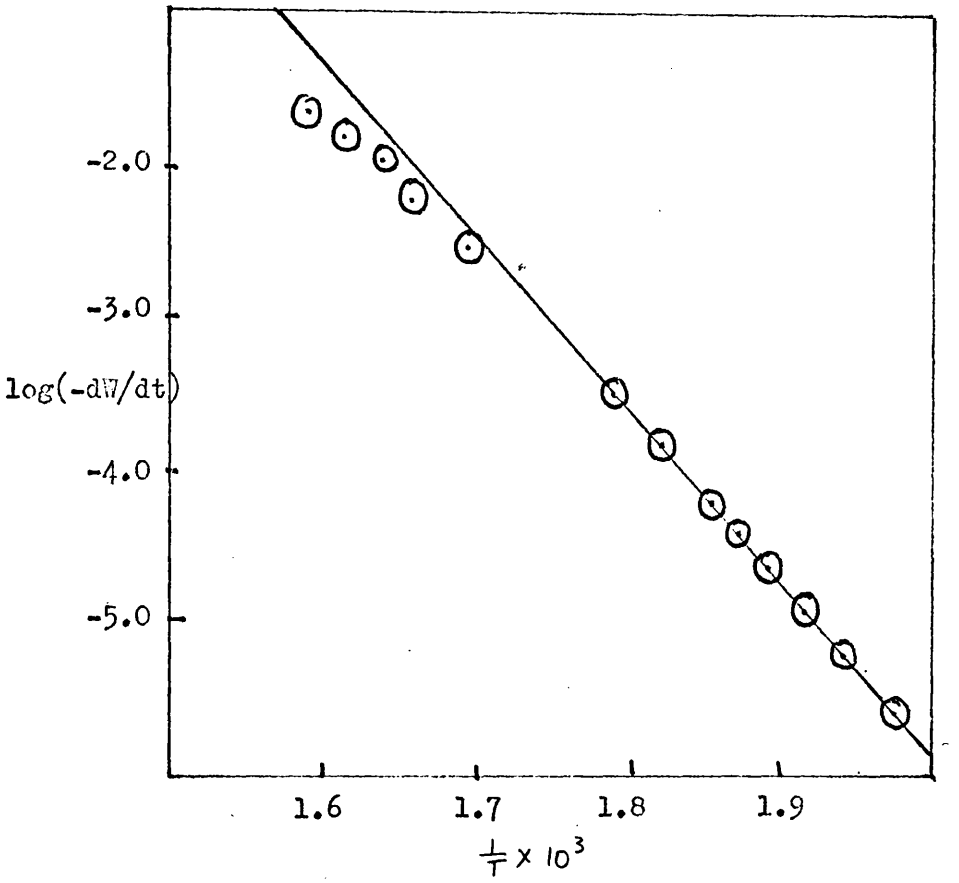
In neglecting weight loss in the early stages of decomposition we are, in effect, ignoring the effect of reaction order "n" on the reaction, or rather assuming that n is zero.

Examination of figure (3,18) shows that in the early stages of the thermogram, order of reaction changes the thermogram only slightly, confirming that the basic assumption of this method is reasonable at low extents of conversion.

In figure (4,6) is shown the result of plotting log rate against reciprocal temperature for a "theoretical" thermogram (obtained as described in Chapter 3, using the computer programme in Appendix II).

As would be expected, the plot is linear over the earlier stage of weight loss, although a significant curvature occurs as the weight loss becomes important.

Providing the Pirani gauge is sufficiently sensitive to detect these early stages of the decomposition where the reaction is independent of order, it should be possible, by a simple plot of log rate (estimated using suitable Pirani calibration graph)

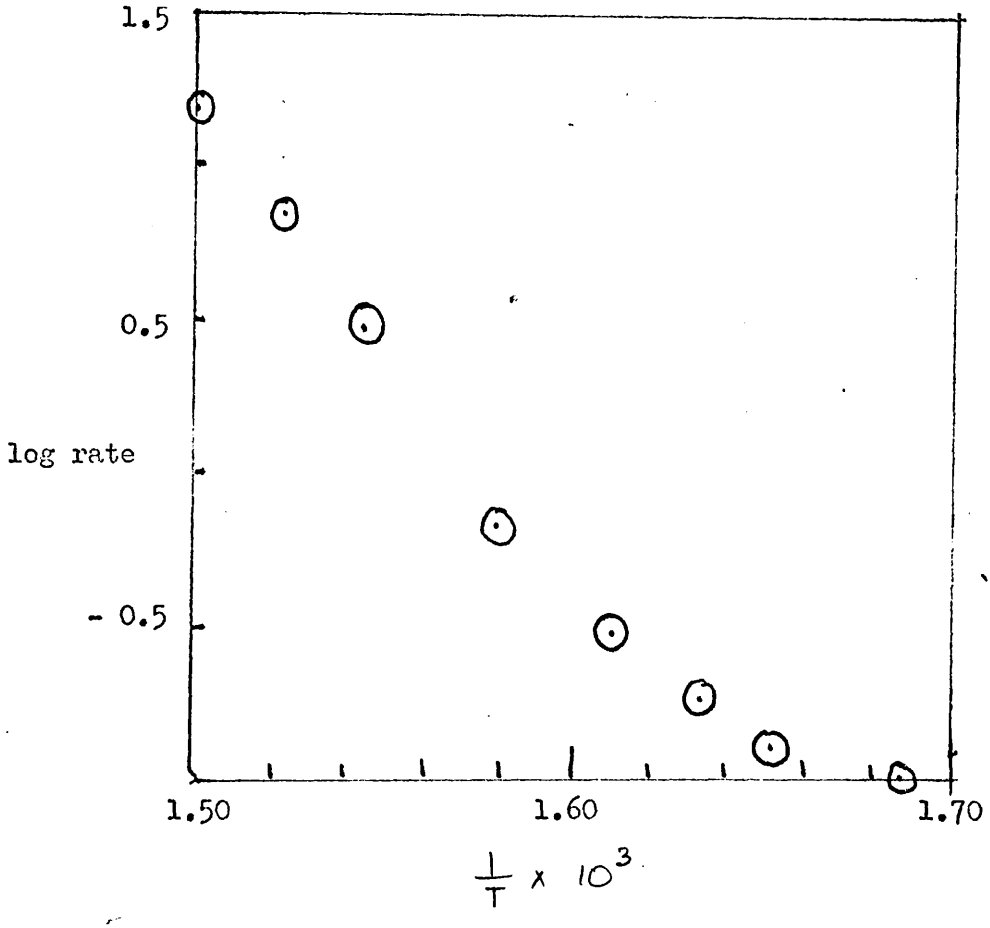


FIGURE(4,6), Plot of log(rate) against 1/T for a "theoretical" thermogram, (E = 50 K.Cal., n = 1), showing the effect on the linearity of the plot of neglecting weight loss

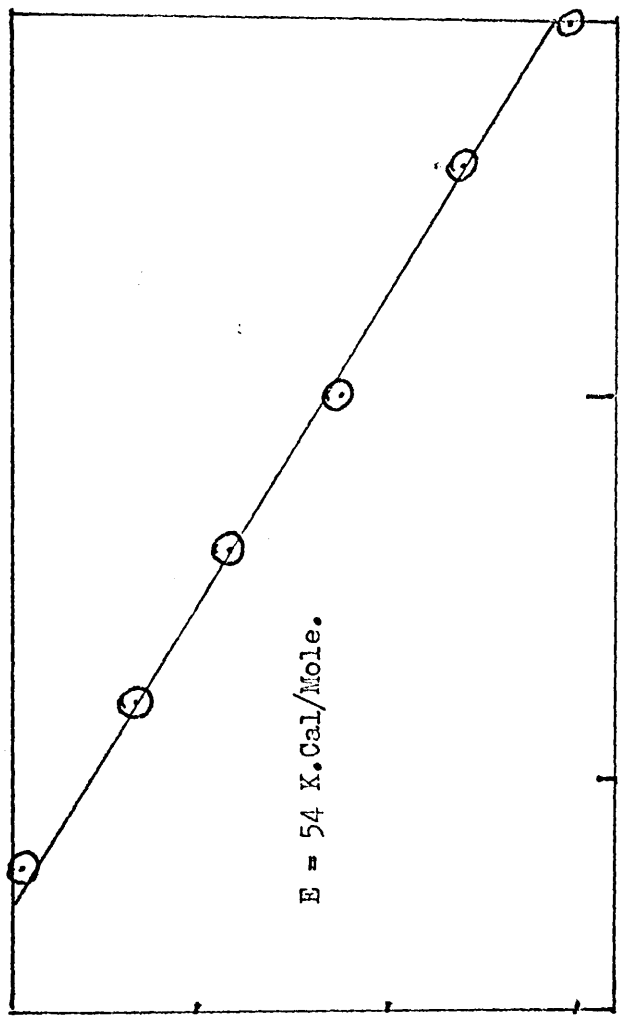
against 1/T (degrees Kelvin), to obtain a linear plot from which E can be estimated. Furthermore, the method has the advantage that the E value so obtained will correspond to the early stages of decomposition, which are frequently of great importance from the point of view of the mechanism of the decomposition (especially the initiation step). It should also be noted that similar plots have been used by Shulman[51] in MTA work.

The result of such a plot for polystyrene NBS 706 is shown in figure (4,7). The graph of log rate against 1/T is clearly non linear, curving in the opposite sense to that predicted by the "theoretical" plot. While this may be due to errors in the Pirani calibration, it is possible that the effect is genuine, and that E for this polymer does increase as degradation proceeds. Certainly, the results of Anderson and Freeman[108] obtained by TG methods, suggest that E values for the early stages of decomposition are less than those obtained at greater extents of conversion.

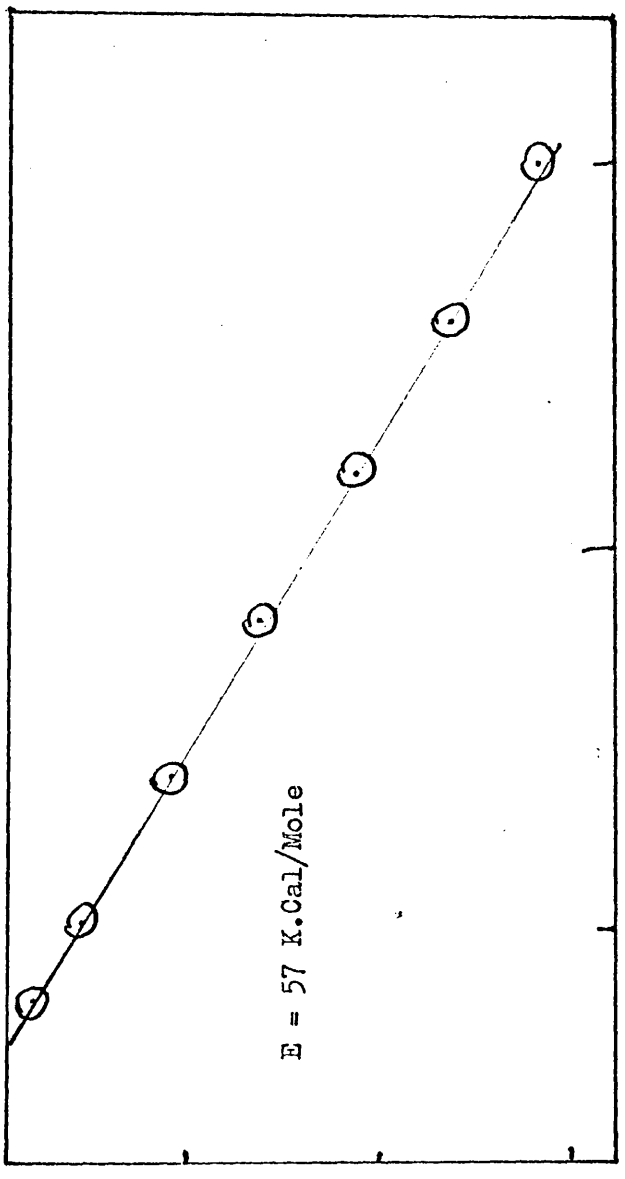
Linear plots were obtained in the case of PMMA FRI, which had been predegraded in order to remove the initial (chain end initiated) TVA peak. As shown in figures (4,8) to (4,10) the energy of activation, as measured by this method, depended upon



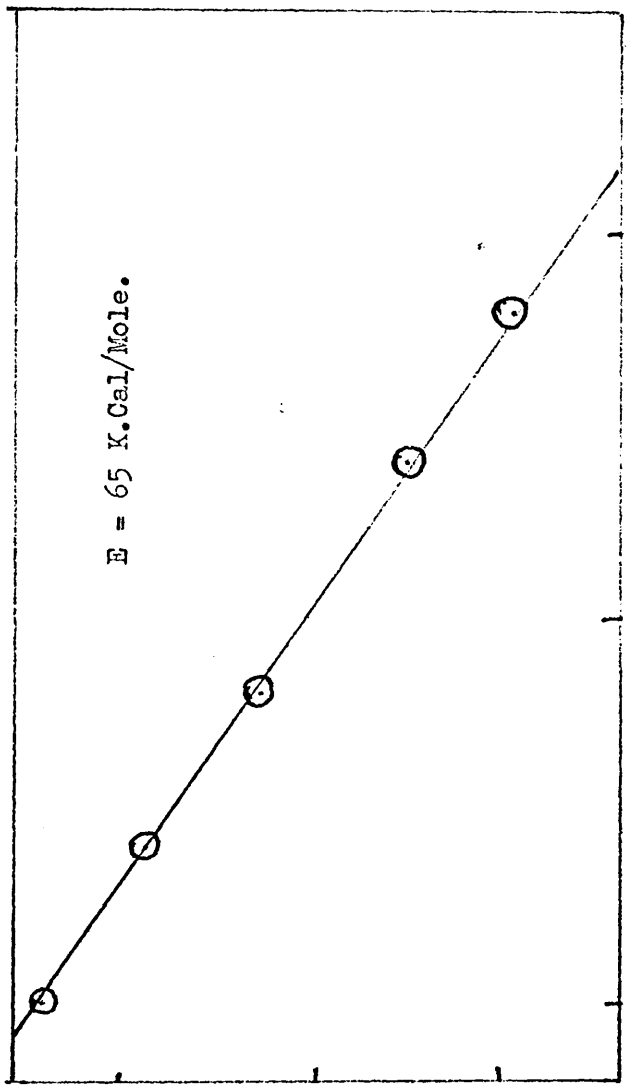
FIGURE(4,7), Plot of log rate (measured from styrene calibration data) against 1/T for Polystyrene NBS 706, showing apparent increase in energy of activation with extent of degradation.
(Rate expressed as g / sec. x 10^{-6})



FIGURE(4,8), Plot of log rate, (from methyl methacrylate calibration data) against 1/T for a sample of PMMA FRI which had been pre-heated at 10^{o}/min to 326^{o}C., and allowed to cool before re- degradation. (Rate expressed as g./sec x 10^{-6})



FIGURE(4,9), Plot of log rate, (from methyl methacrylate calibration data) against $1/T$ for a sample of PMMA FRI which had been pre- heated at 5^{o}/min to 330^{o}C., and allowed to cool before re-degradation.
(Rate expressed as g./sec x 10^{-6})



FIGURE(4, 10), Plot of log rate (from methyl methacrylate calibration data) against 1/T for a sample of PMMA FRI which had been pre-heated at 10°/min to 346°C., and allowed to cool before re-degradation.
(Rate expressed as g./sec x 10^{-6})

the extent to which the preheating was carried out. As the preheating time was increased, the energy of activation also increased. This increasing thermal stability is almost certainly due to the progressive removal of unstable end structures by preheating. The greater the extent of preheating, the less the number of such end structures remaining. A similar increase in thermal stability with extent of degradation has been observed by Grassie[3] and Jellinek[109].

Unfortunately, since the energy of activation for this polymer is dependent on molecular weight, as well as extent of degradation, the absolute values obtained in this work can not be regarded as particularly significant.

Kinetic Data, Using Entire Thermogram.

The method described above is restricted to the early stages of decomposition, and E is the only parameter obtainable by this method.

However, equations developed by Friedman[111], permit the determination of A, E and n from a TVA thermogram, providing prior calibration of the Pirani gauge for the evolved substance, has been carried out.

Since at the time of writing this thesis, these equations have not been published, the method proposed by this author

requires explanation in some detail, and by permission of the author is shown below.

The equation of a TVA thermogram (see page 111) can be written:

$$-1/Wo\ (dW/dt) = A\ (W/Wo)^{n} \exp\ (-E/RT). \qquad (4,e).$$

whence $\log A = \log\ (-dW/dt) - \log Wo + E/2.303\ RT - n\log\ (W/Wo).$ (4,f).

Assuming the kinetics of the process do not change during the TVA peak, this expression should hold at all points on the thermogram, say 1 and 2.

Thus $\log A = \log\ (-dW/dt)_1 - \log Wo + E/2.303\ RT_1 + n\log\ (W_1/Wo)$ (4,h)

and $\log A = \log\ (-dW/dt)_2 - \log Wo + E/2.303\ RT_2 + n\log\ (W_2/Wo)$ (4,j)

Hence- $$E/2.303R = \frac{\log\ (-dW/dt)_2/(-dW/dt)_1 + n\log\ (W_1/W_2)}{(1/T_2) - (1/T_1)} \qquad (4,k)$$

Similarly, for a point 3,

$$-E/2.303R = \frac{\log\ (-dW/dt)_3/(-dW/dt)_1 + n\log\ (W_1/W_3)}{(1/T_3) - (1/T_1)} \qquad (4,m)$$

It follows that the reaction order n is given by

$$n = \frac{\log \frac{(-dW/dt)_3}{(-dW/dt)_1} - \frac{T_2\,(T_3 - T_1)}{T_3\,(T_2 - T_1)} \log \frac{(-dW/dt)_2}{(-dW/dt)_1}}{\frac{T_2\,(T_3 - T_1)}{T_3\,(T_2 - T_1)} \log (W_1/W_2) - \log (W_1/W_3)} \qquad (4,n)$$

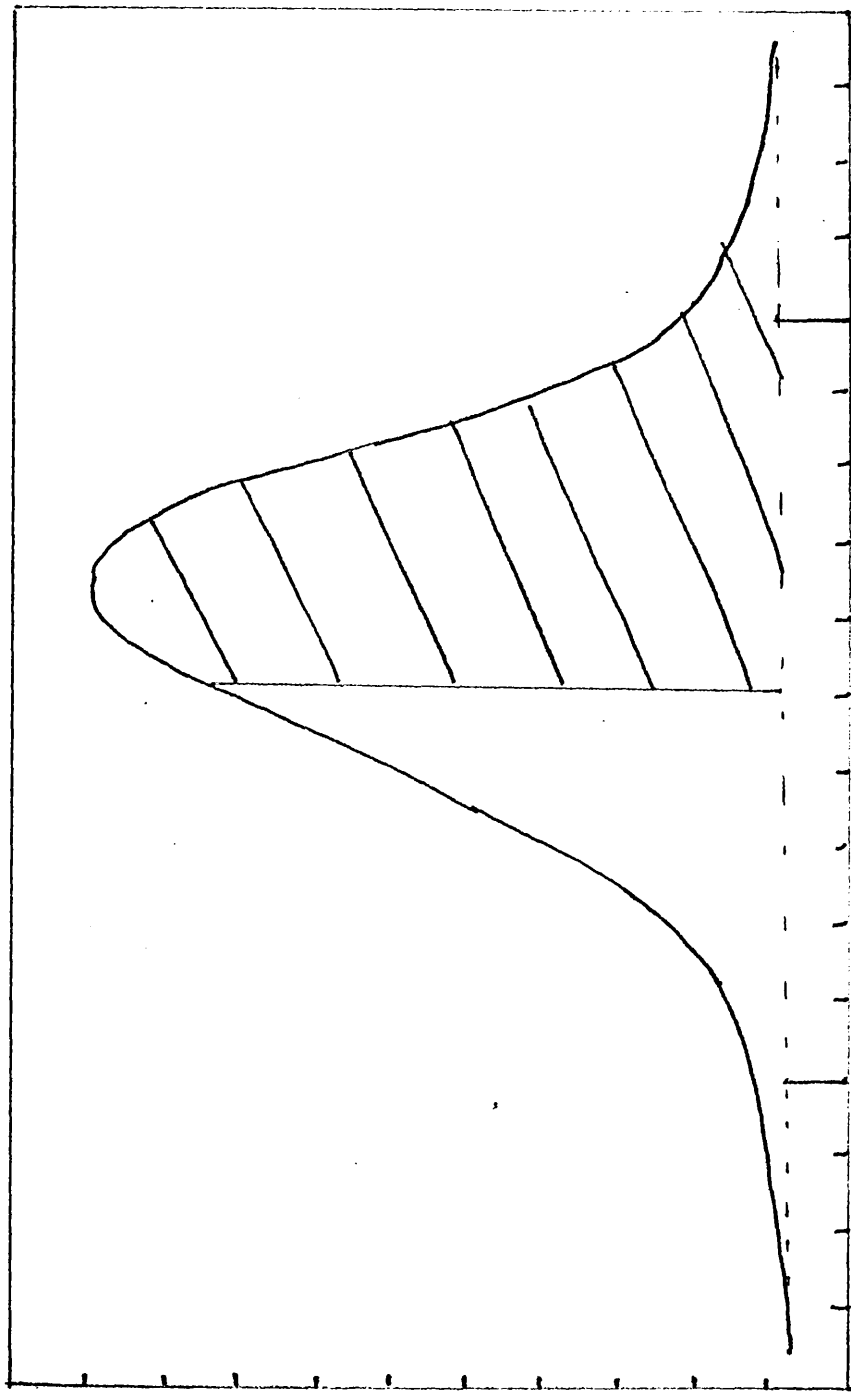
where Wo = initial reactive weight = constant x area under thermogram.

W = reactive weight remaining at temperature T.

Thus once n has been determined, E and A can be obtained using equations (4,k) and (4,h).

Friedman has also suggested several simplifications of the basic equations, and has shown that when applied to a "theoretical" differential thermogram, the results obtained are in excellent agreement with the expected values.

This method was applied to the thermogram for the decomposition of 1 mg. of PMMA FRI which had previously been degraded at 10°/min to 320°C. The points T_1, T_2, T_3 were chosen as shown in figure (4,11), W in each case being estimated from the area under the mV- temperature plot. It was assumed that the rate of sample decomposition was linear with Pirani response (the peak height falls below 2 mV). The values obtained found to be n = 1.1, E = 52 K Cal/mole, A = 10^{16} (A plot of log(rate) against 1/T gave, E = 50 K Cal/mole). The two methods are therefore in reasonable agreement.



FIGURE(4,11), Thermogram used for Friedman method of obtaining kinetic data. (W_3 = shaded area.)

OTHER METHODS OF OBTAINING KINETIC DATA FROM TVA TRACES.

Several methods have been suggested by Cameron and Fortune (105) for determining kinetic parameters from TVA curves, each method relying upon the determination of Tmax. The application of the Kissinger equation, (4,d) has been illustrated earlier in this Chapter. However, although methods based upon determination of Tmax are sound, in principle, the scatter of points observed in figures (4,1) to (4,5) is due to the difficulty of estimating Tmax accurately, say to the nearest degree. Until methods of temperature measurement are improved considerably, methods based upon the precise determination of a single temperature will be difficult to apply.

The other methods recommended by these authors for use in TVA, in addition to the accurate estimation of Tmax, require that the Pirani gauge be calibrated beforehand, and are limited to situations where the exponent n is 1, or has been determined independently. In addition, two expressions involve the use of the quantity Wo (referred to as initial weight, but more correctly, should be initial reactive weight, = (Wi - Wf)). The authors suggest that Wo could be determined by weighing the polymer sample before degradation. This requires that the sample be free of occluded solvent, and that it should decompose completely by a

single stage process (i.e. give a TVA thermogram with a single peak). In fact, where 100% weight loss does not occur, the polymer sample must be weighed before, and after degradation, which precludes the use of small samples.

It would appear then, that the methods outlined by these authors have no advantage over the method suggested by Friedman, which although suffers from the drawbacks of any single point method, is not so severely limited with respect to the value of n.

FUTURE DEVELOPMENTS.

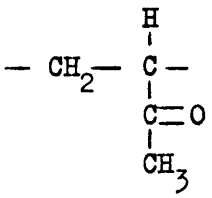
An obvious future development in the quantitative application of TVA is the use of DCTVA to estimate kinetic parameters for the formation of non condensable products. The Pirani gauge could be calibrated by using the plot of initial sample weight against Pirani output at a particular temperature, in order to obtain relative rate values, as described in Chapter 3 (page 101).

Much of the tedious calculation could also be eliminated from this work by the use of computer techniques, whereby several methods of obtaining kinetic parameters could be applied to a single set of data, and the results compared.

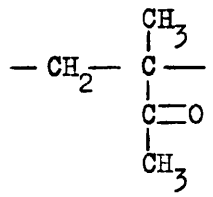
CHAPTER FIVE.

THE THERMAL DEGRADATION OF POLY (METHYL VINYL KETONE) AND POLY (METHYL ISO-PROPENYL KETONE).

Poly (methyl vinyl ketone) PMVK, and poly (methyl iso-propenyl ketone) PMIK, have the structures (1) and (2) respectively:-



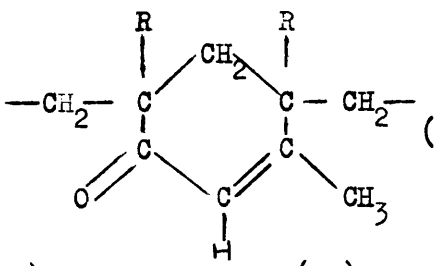
PMVK. (1)



PMIK. (2)

Some interest has already been taken in the degradation of these polymers, the earliest work being that of Marvel and co-workers [56,57], who showed that the polymers had a "head to tail" arrangement of monomer units, yielding water and a cyclohexenone ring system (3)on heating:-

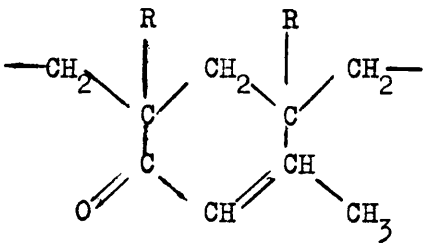
PMVK or PMIK $\xrightarrow[-\ H_2O]{\text{HEAT}}$



(R = CH_3 or H).

Grassie and Hay [18,58], and Matzuzaki [59] confirmed the earlier findings and, by study of the C:H:O ratio in the residue [58,59], infra-red [18,59] and ultra-violet absorption spectroscopy [58,59] showed that the residue was converted, on heating, to structures

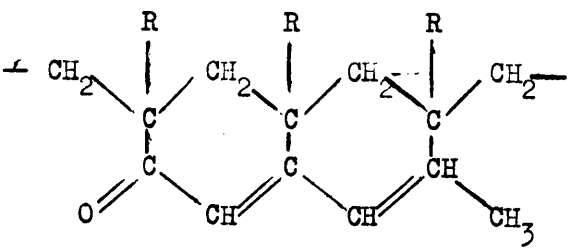
of the type B, C and D shown below:-



(B)

R=H max. = 235 mμ (58)

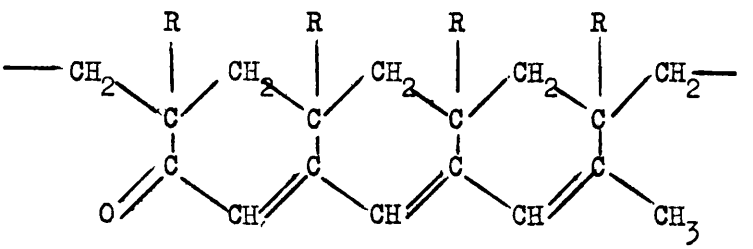
$R=CH_3$ max. = 240 mμ (59)



(C)

R=H max. = 285 mμ (58)

$R=CH_3$ max. = 292 mμ (59)



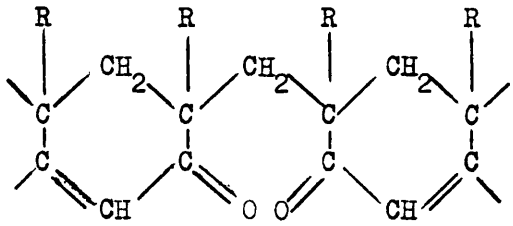
(D)

R=H max. = 335 mμ (58)

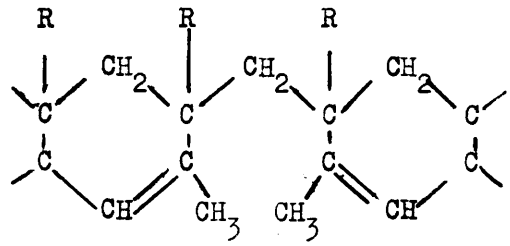
$R=CH_3$ max. = 340 mμ (59)

The yellow coloration which the residue acquired was believed to be due to structures of type B, C and D. Wall [60] and Hay [58] have pointed out that by contrast with polyacrylonitrile [15,16] the random nature of the cyclisation process in PMVK and PMIK means that not all the oxygen can be eliminated from the polymer as water. This is due to the formation of "incompatible"

structures, such as E and F, shown below, which prevent the cyclisation process from proceeding along the entire length of the molecule:-



(E)



(F)

The work reviewed above clearly established the following points:-

(a) The polymers have a "head to tail" structure.

(b) Both polymers, on heating, undergo an intramolecular condensation of adjacent pendant groups, eliminating water by a mechanism which is probably analogous to that of the "aldol" condensation reaction [18].

(c) This reaction is random in nature so that side chains react in "clusters" rather than the cyclisation passing through the length of the molecule. As a consequence, 79% to 85% of the oxygen is lost as water from PMVK, and 63% of the oxygen is eliminated from PMIK under similar conditions [57]. Some aspects of the thermal degradation of these polymers listed below, have not been fully elucidated, however:-

(1) Unzipping of the PMIK chain to monomer might be expected by analogy with other 1:1 disubstituted polymers. For example, both polyacrylonitrile and polymethacrylonitrile undergo coloration reactions. In the case of the latter, however, monomer yields of up to 100% have been reported, when the polymer prepared was free of methacrylic acid units [21,33]. Similarly, poly (methyl methacrylate) decomposes quantitatively to monomer, while monomer yields from poly (methyl acrylate) are negligible [10].

Monomer was detected by Marvel [57] in the pyrolysis products of PMIK. It was not established, however, whether this was a major product.

(2) It was not clearly established in what way the additional methyl group in PMIK affected the rate or extent of cyclisation in the two polymers.

(3) The thermal stability of the condensed ring system formed by water elimination, was not examined. It is of interest to observe whether or not cyclisation leads to the formation of a stable residue akin to that formed in the pyrolysis of polyacrylonitrile. It was hoped that study of the polymers using TVA might help to clarify these points.

PRELIMINARY EXPERIMENTS.

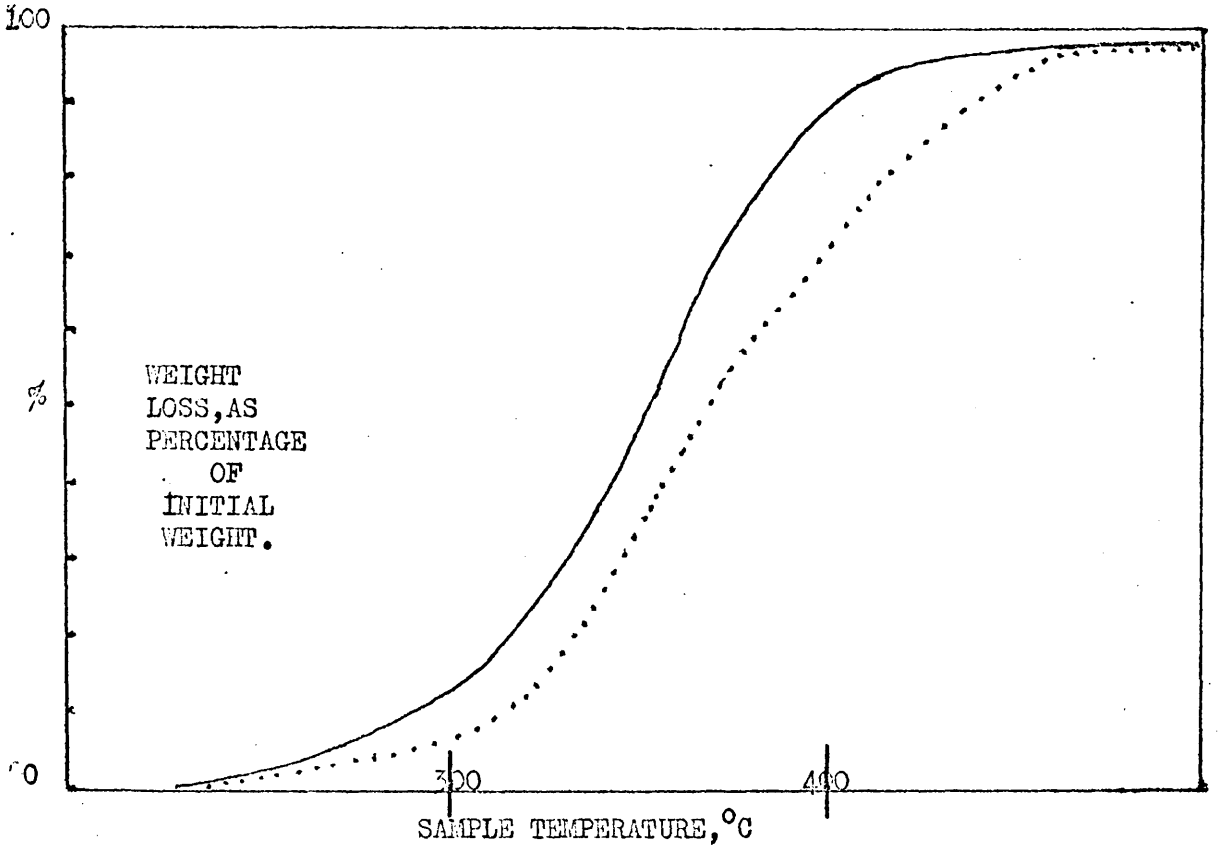
Three samples of each polymer were prepared for this study,

the details of preparation being given in Appendix 1. The PMVK samples were rubbery, clear and soft, soluble in ketonic solvents but insoluble in benzene or toluene. The PMIK samples were white powders, and were also insoluble in aromatic solvents.

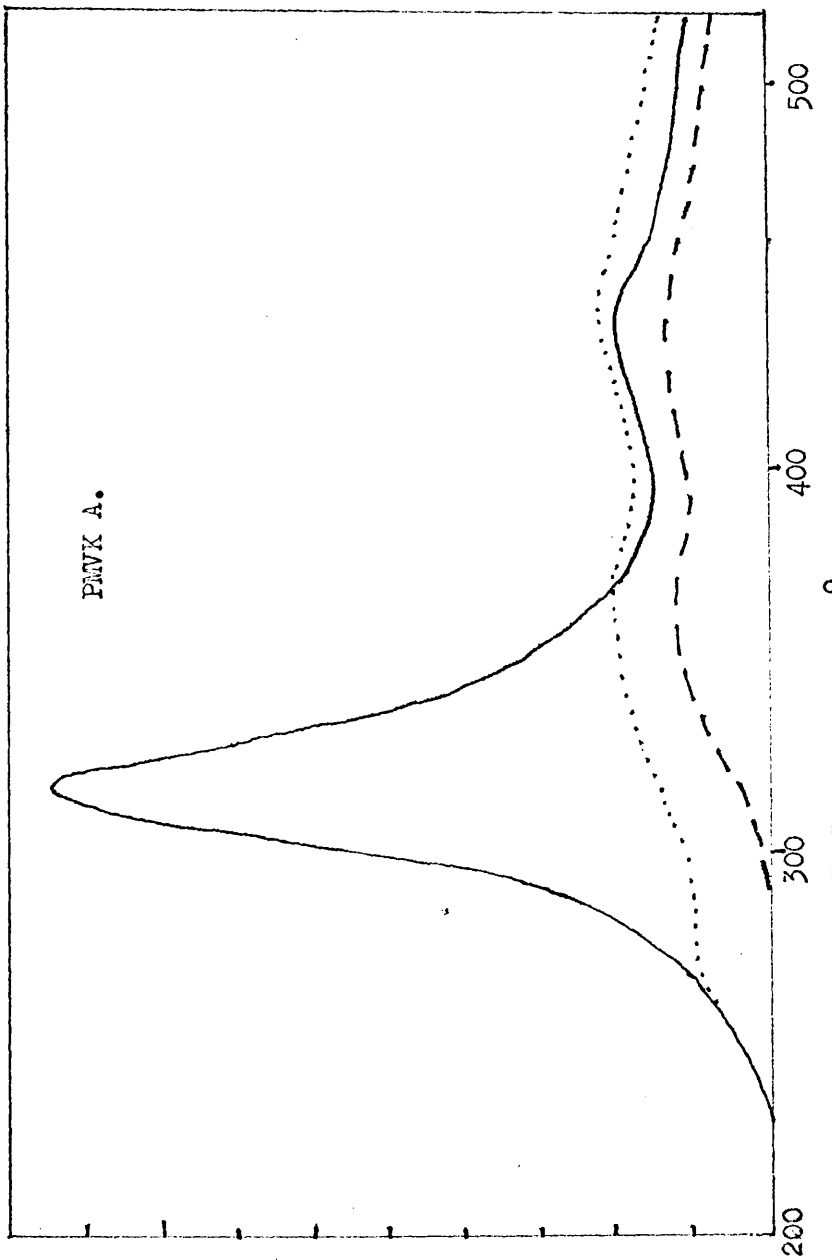
TG thermograms for a PMVK and a PMIK sample are shown in figure (5,1). The other samples of PMVK and PMIK behaved in a similar fashion to those chosen for the diagram. Clearly, PMIK is less stable than PMVK, although both polymers degrade to approximately the same final percentage residue. The residue of both polymers was found to be stable in the temperature range 500 to 800°c.

Thermograms for the polymers were obtained using the normal TVA system (Pirani gauge between sample and cold trap), but these did not give any clear indication of the processes occurring in the decomposing polymers. In figures (5,2) to (5,7) are shown thermograms obtained using the Differential Condensation apparatus. Comparison of the thermograms reveals the following points:-

(1) No monomer is evolved in the thermal decomposition of PMVK. In the main degradation peak, the trace for the Pirani placed beyond the - 75° trap shows the typical behaviour of water in the system, the slow distillation of water from the - 75° trap to the liquid nitrogen trap showing as an output of 0.2 to 0.3 mv on the Pirani. If monomer had been a major product, it would have

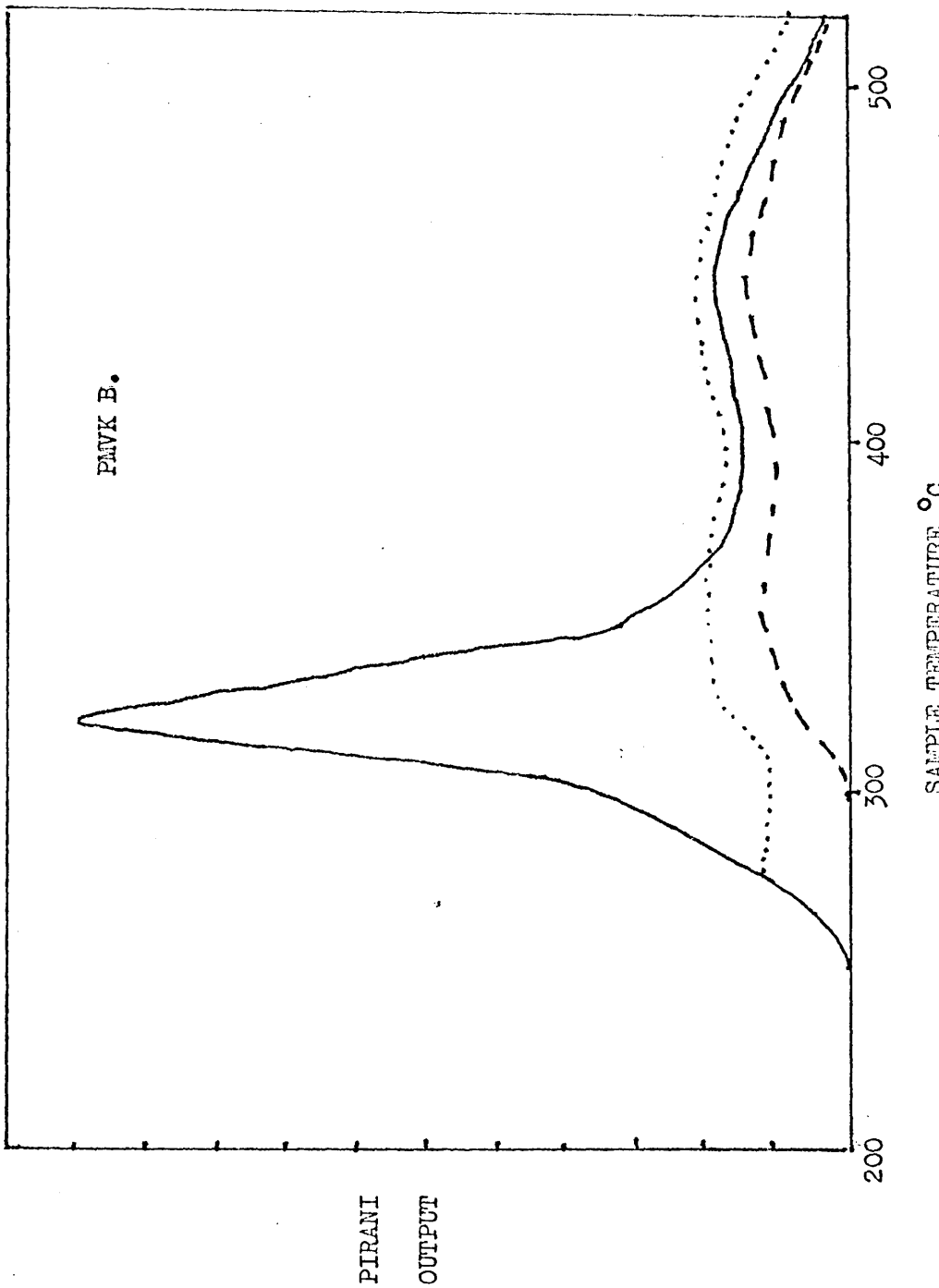


FIGURE(5,1), TG Thermograms for PMIK F$_0$ (full line), and PMVK A (dotted line), at a heating rate of 10°/min., in a nitrogen atmosphere (rate of flow 60ml./min.), using a platinum sample crucible.
Experiments conducted on a Du Pont TG Instrument (model 950)

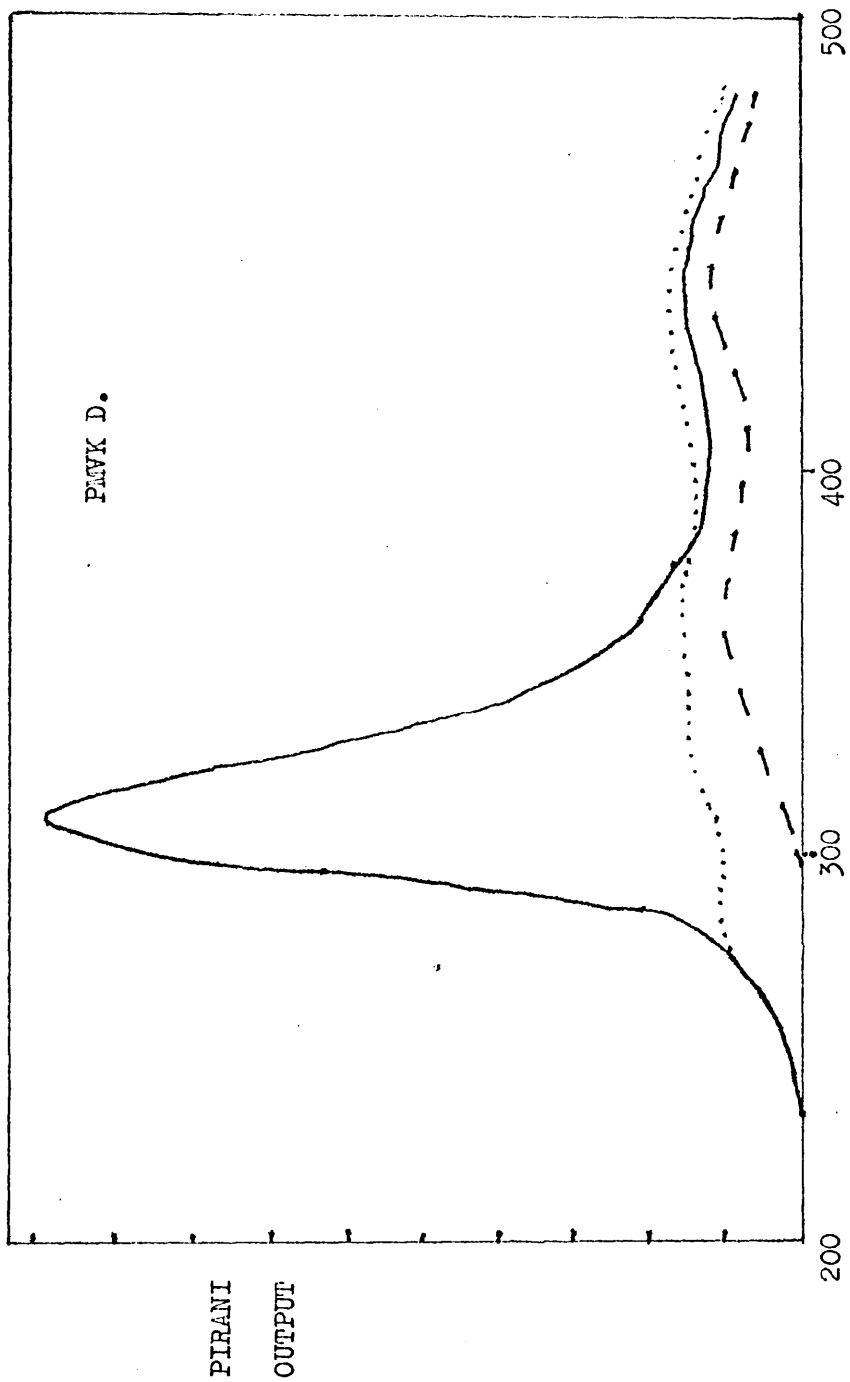


FIGURE(5,2) DC-TVA Thermogram for a 50mg Sample of PMVK A, at a heating rate of 10°/min. Sample as thin slices.

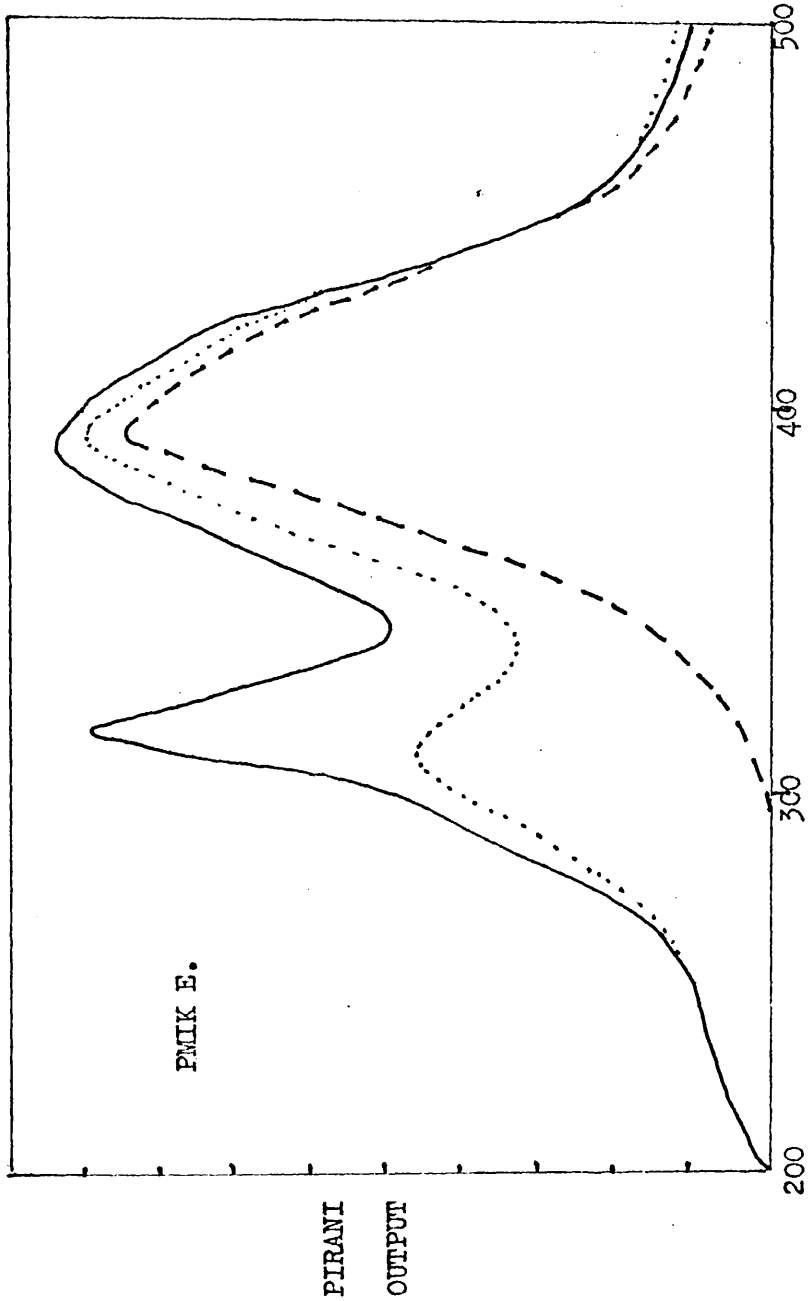
— — — Output from gauge head placed after a cold trap at -100°C
. . . . . Output from a similar gauge head, trap at -75°C
——— Outputs from gauge heads after traps at 0°C and -45°C.



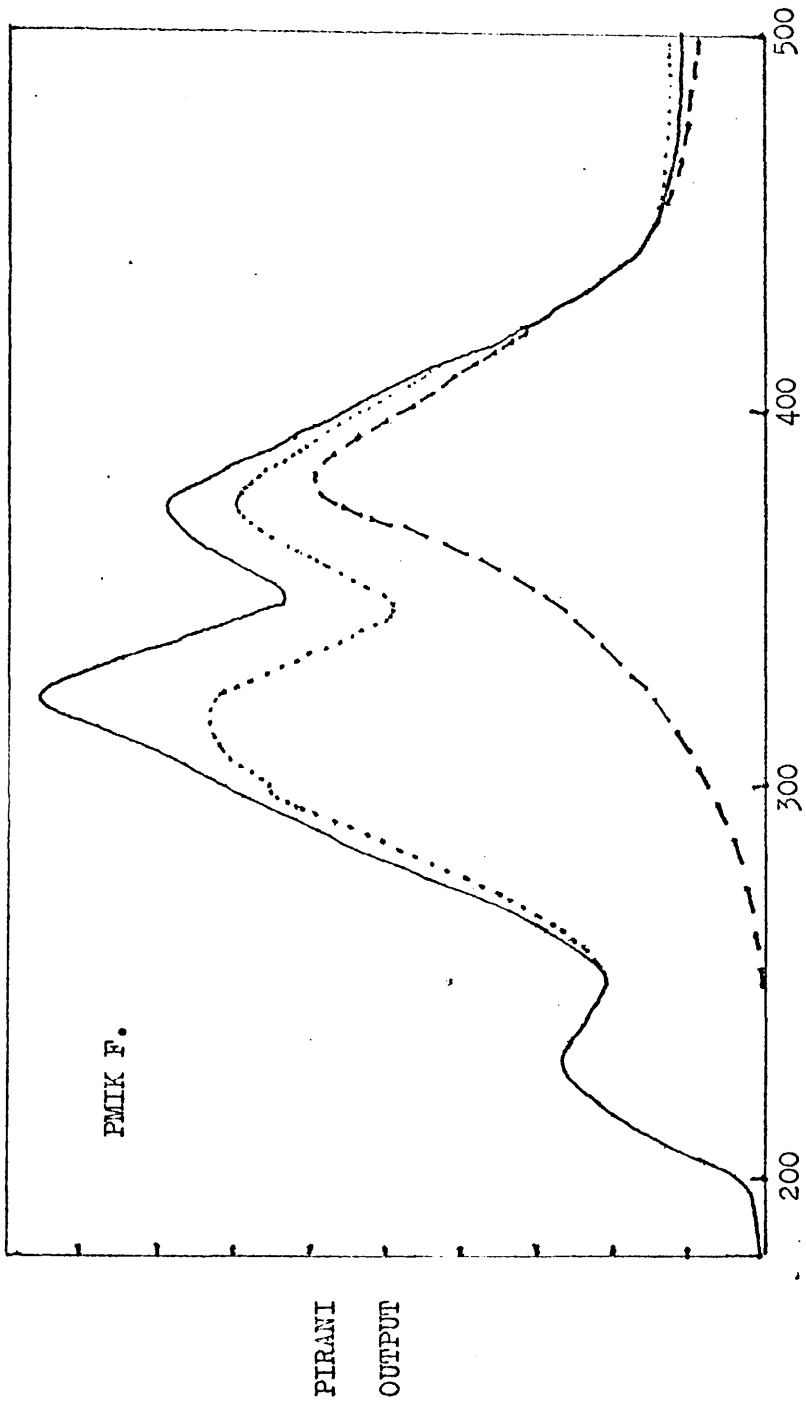
FIGURE(5,3), DC-TVA Thermogram for a 50mg sample of PMVK B, under the same experimental conditions as those used for PMVK A (Figure(5,2))



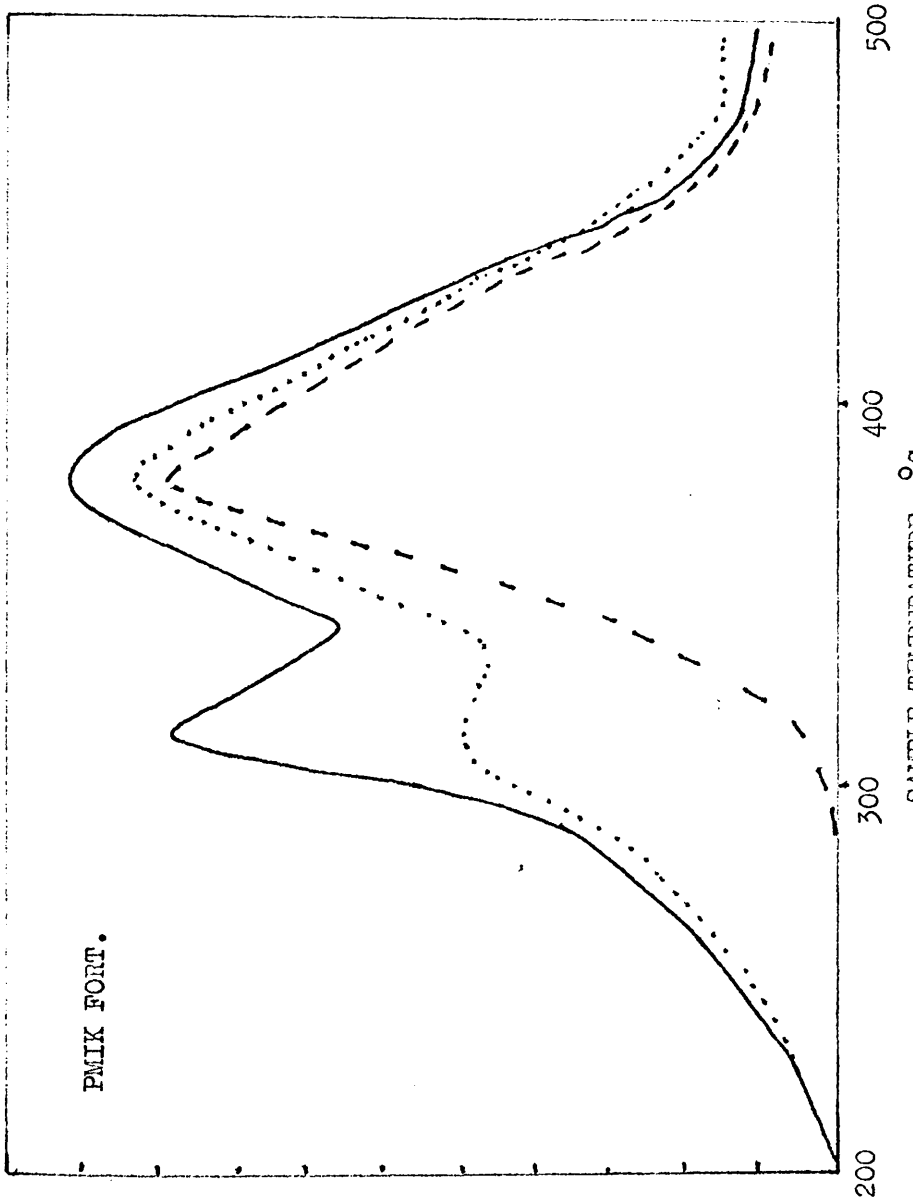
FIGURE(5,4), DC-TVA Thermogram for a 50mg sample of PMVK D, under the same experimental conditons as for PMVK A (Figure(5,2))



FIGURE(5,5), DC-TVA Thermogram for a 50mg sample of PMIK E, under the same experimental conditions as those used for PMVK samples (Figure(5,2)), sample as a fine powder.



FIGURE(5,6), DC-TVA Thermogram for a 50mg sample of PMIK F, underthe same conditions as for PMIK E, (Figure(5,2))



FIGURE(5,7), DC-TVA thermogram for 50 mg sample of PMIK FORT., under the same conditions as for PMIK E. (Figure(5,5)).

appeared on the - 75° trace, since it is not condensed at this temperature. (See Chapter 2, table 2,3).

This is in agreement with the conclusions reached by Hay [61], who showed that water was the only product at 250°C in isothermal experiments.

(2) In PMIK, however, as much as 50% of the first peak is caused by material which is not condensed at - 75°C. Although no data is available on the behaviour of methyl isopropenyl ketone in the Differential Condensation apparatus, product analysis shows this unknown material to be monomer (see later section of this Chapter).

(3) Beyond the first peak of the thermogram, the decomposition of both polymers is accompanied by the production of material which is not condensed at - 100°C. For the same initial weight of material, it is apparent that a greater amount of non condensable material is evolved from PMIK than from PMVK.

At the end of an experiment, it was found that the upper portion of the degradation tube was covered with a brown ring, the nature of which is discussed below. Interruption of the degradation at various temperatures established that in both polymers this product fraction began to appear just after the maximum of the first degradation peak had been passed.

It was also observed that both polymers had yellowed

noticeably at temperatures as low as 220°C, i.e. before the onset of the main degradation peak.

PRODUCT IEDNTIFICATION.

The degradation products from PMVK and PMIK can be classified into groups:-

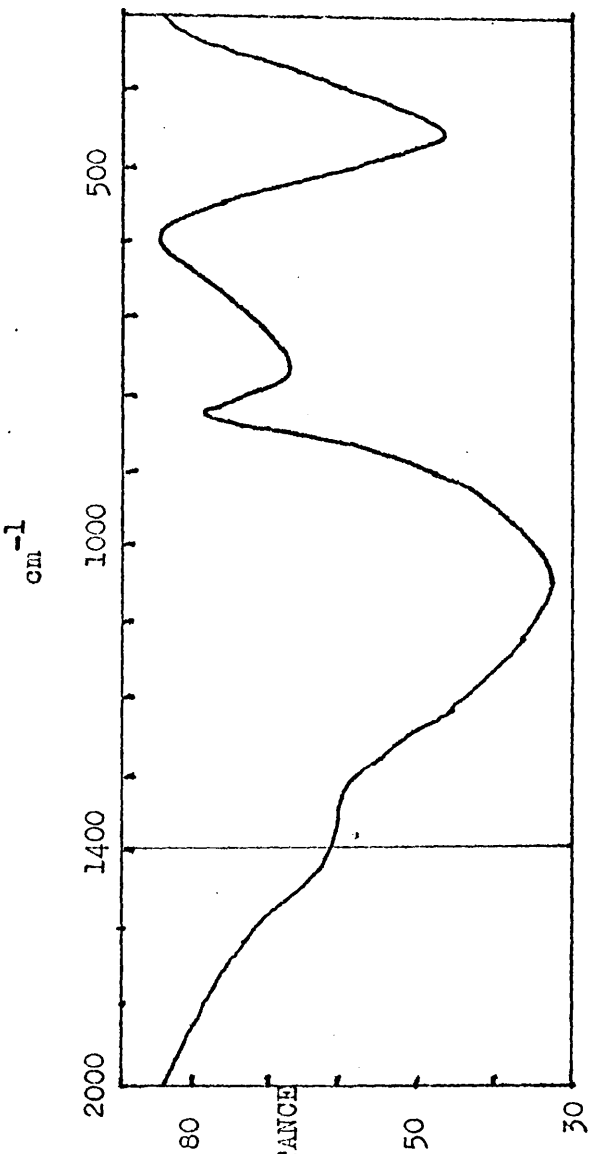
(a) The involatile residue comprising products involatile at 500° under vacuum.

(b) The cold-ring fraction, which consists of products volatile at degradation temperatures, but involatile at room temperature, under vacuum.

(c) Products condensable at - 100°C.

(d) Products not condensed at -100°C.

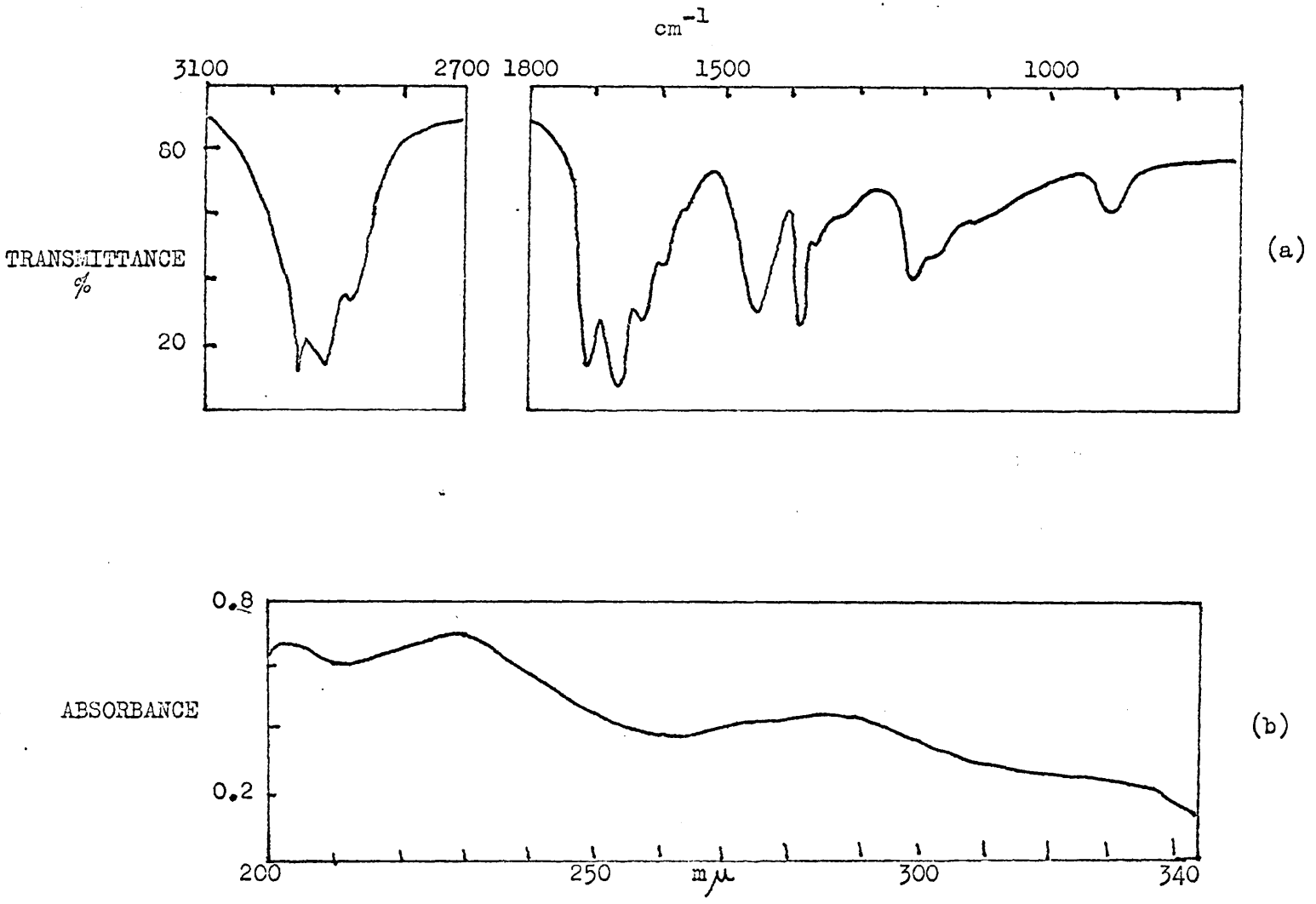
(a) The structural changes occurring in the residue as a result of the intra molecular cyclisation reaction have been thoroughly investigated [58,59], and have been discussed above. The structure of the residue remaining at 500°C was examined, in the case of PMIK, by infra-red spectroscopy, the spectrum being shown in figure (5,8). This spectrum indicates that all carbonyl groups have been eliminated from the polymer, and that the residue is probably an impure form of carbon. Presumably the residue from PMVK degradation is similar, although it was not possible to isolate a suitable sample of the residue for infra-red analysis.



FIGURE(5,8), Infra-red spectrum of the residue remaining from degradation of PMIK F to 500°C, sample as fine powder, pressed into KBr disc.

(b) The nature of the cold-ring fraction was examined by infra-red and ultra-violet spectroscopy. The upper portion of the degradation tube was wiped with a tissue moistened with the appropriate solvent (A.R. carbon tetrachloride for I.R., "Spectrosol"hexane for U.V.) and the tissue then extracted with a further portion of the same solvent, and a spectrum taken of the extract. The spectra obtained in this way from the PMIK cold-ring are shown in figure (5,9). The corresponding spectra for PMVK were almost identical. U.V. peaks at 230 and 280 mμ suggest that groupings of type B and C (see page 147) are present in this product fraction. Slight absorption in the region 330-335 mμ may be attributable to D type ring formations. The I.R. spectrum is consistent with unsaturated six membered ketone rings.

(c) The products from the pyrolysis of PMIK which were condensable at - 100°C, were trapped out at this temperature and distilled into a capillary tube reservoir. On thawing out, the products separated into two layers of approximately equal volumes. When the reservoir was opened a strong smell of monomer was observed. The lower liquid layer was water miscible, while the upper layer was organic. Since water was evidently present, it was removed by shaking the products with "analar" carbon



FIGURE(5,9), Infra- red spectrum (a), and ultra-violet spectrum (b), of "cold-ring" fraction from degradation, to 500°C, of PMIK F.

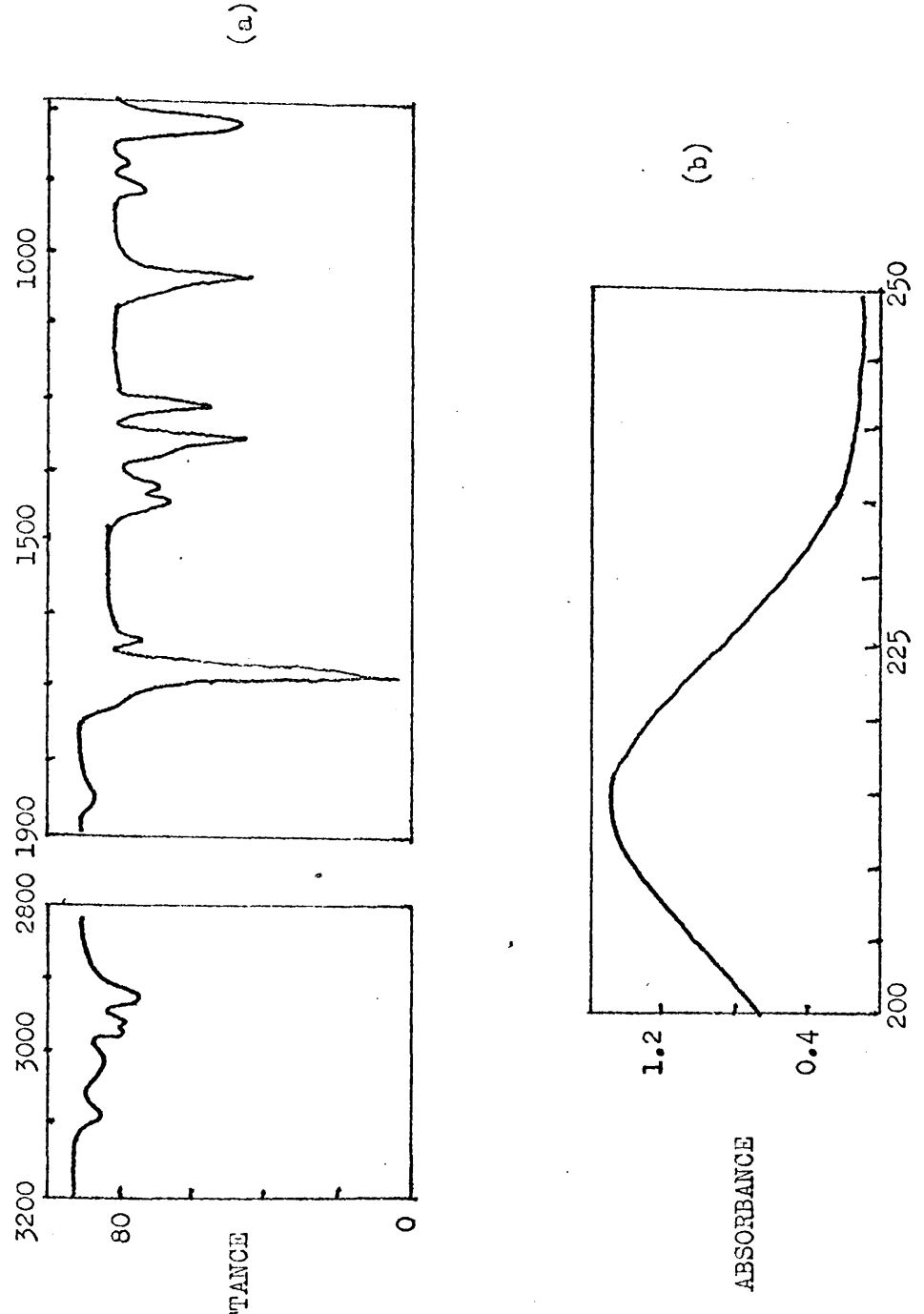
tetrachloride containing anhydrous magnesium sulphate, before an infra-red spectrum was taken. In a similar fashion, the liquid was dried before an ultra-violet spectrum in hexane was run. These spectra are shown in figure (5,10).

The infra-red spectrum is identical to that for methyl isopropenyl ketone [62], while the λ max value of the U.V. absorption is in good agreement with the literature value for this compound [63].

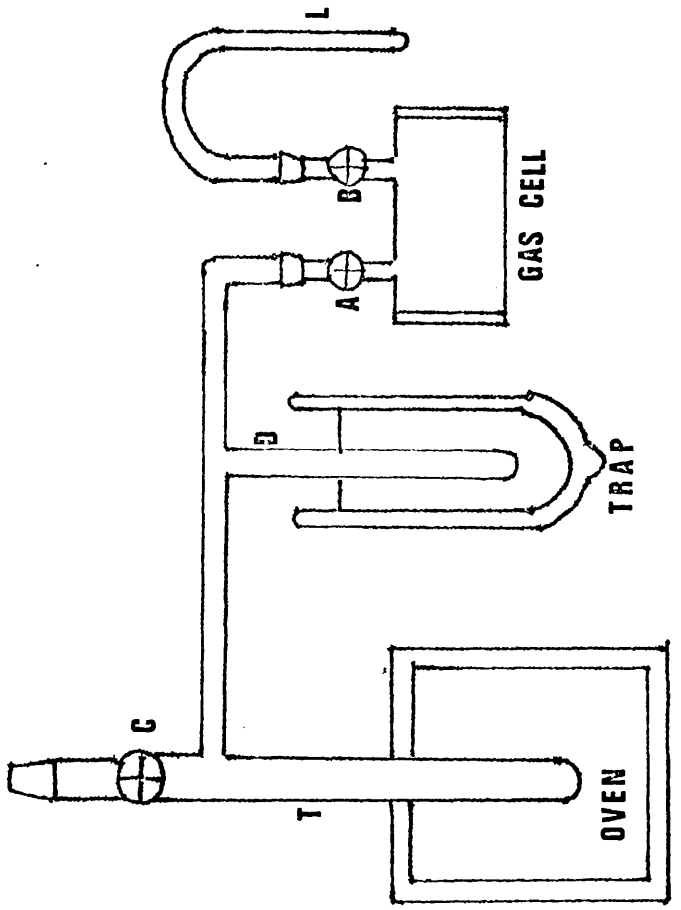
The identity of the material not condensed at - 75°C in the TVA thermogram of PMIK is thus clearly established as monomer.

By contrast, the liquid products from PMVK degradation were not found to contain monomer,

(d) The identity of the product fraction which was not condensed at - 100°C was established for each polymer, using the closed degradation system shown in figure (5,11). 200 mg of the polymer was placed in tube T, and the system was then evacuated through the 4 mm. stopcock C, taps A and B being open. All the taps were then closed, and the system was clamped in position so that the lower portion of tube T was in the TVA oven. A cold-trap at - 100°C was placed around the cold finger D, and the sample was heated at 10°/ min to 500°C, and then allowed to



FIGURE(5,10), Infra-red spectrum (a), and ultra-violet spectrum(b),of liquid products from pyrolysis of PMIK F, after removal of water.



FIGURE(5,11), Apparatus for collection of non - condensable products.

cool.Taps A and B were then opened and L was immersed in a liquid nitrogen bath. After five minutes A was closed, the cold-trap was removed, the gas cell disconnected from the system, and a spectrum was taken. This is shown for the product fraction from PMIK in figure (5,12). The characteristic band spectra of methane and carbon monoxide are clearly evident. The PMVK spectrum differed only in that the intensities of the peaks were somewhat reduced.

INTERPRETATION AND DISCUSSION OF RESULTS.

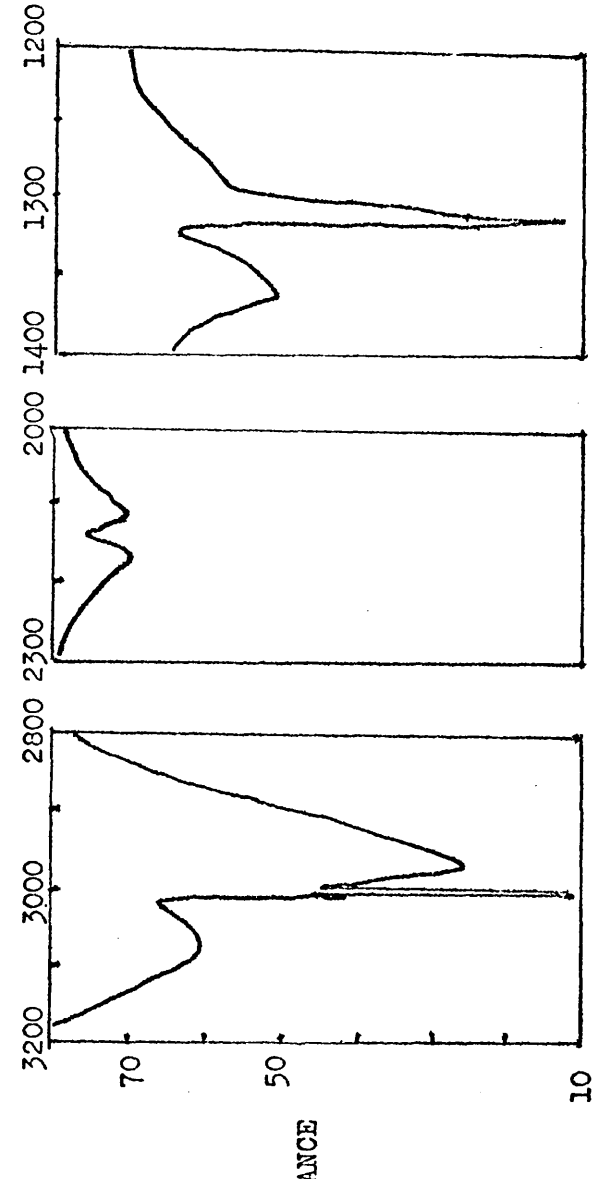
The salient points emerging from the foregoing experiments are:-

(1) The production of monomer forms an important part of the thermal decomposition behaviour of PMIK. Up to 50% of the liquid products are methyl iso-propenyl ketone.

(2) The production of carbon monoxide and methane, which occurs above 300°C in both polymers, is a more important reaction in the case of PMIK samples.

Monomer Production in PMIK.

By analogy with polymers of other 1:1 disubstituted monomers, the production of monomer from PMIK is not unexpected. Indeed the TVA thermograms suggest that in the early stages of decomposition, monomer is the major product (the 0°, - 45° and 75° Pirani traces



FIGURE(5,12), Infra-red spectrum of the non-condensable products from degradation of PMIK F (Fine structure omitted in transcription.)

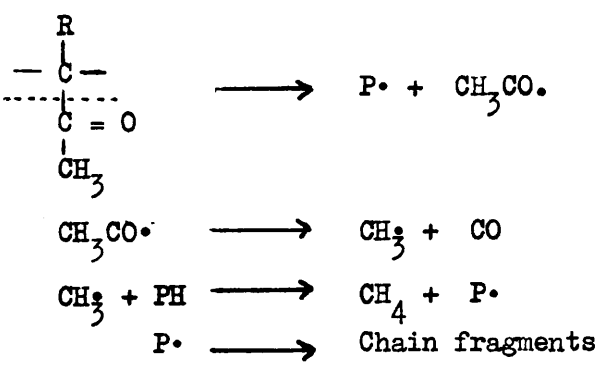
are, at this stage, coincident). Gradually, however, the - 75° trace falls below the others, indicating the increasing rate of water elimination. The T max for monomer production comes before that of the 0° and - 45° traces, indicating that monomer production is a separate process from the cyclisation of pendant groups.

Depolymerisation is presumably prevented from going to completion by the formation of structures such as B, C and D (see page 147) which do not permit the unzipping reaction to pass through them.

Formation of Methane and Carbon Monoxide.

Above 350°C, the production of carbon monoxide and methane from PMIK is clearly a major process, and is indicated in the TVA thermogram by the rise in the trace for material which is not condensed at - 100°C.

A possible mechanism for the production of these compounds is shown below:-



where PH and P• denote a polymer molecule and polymer radical, respectively.

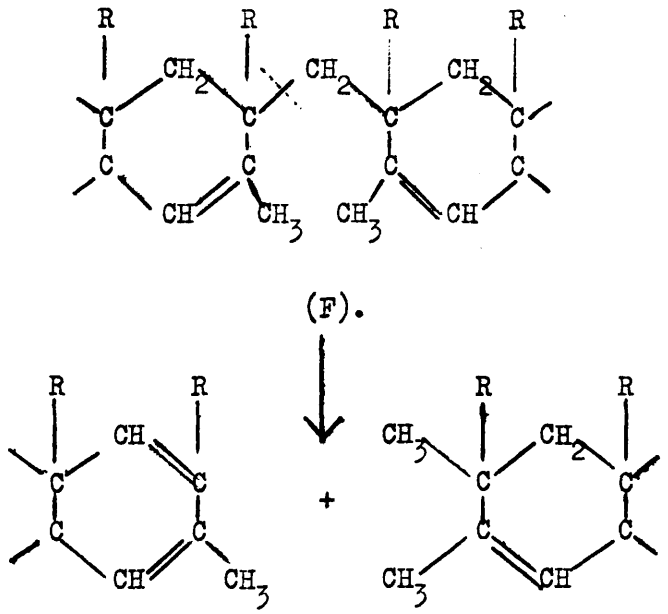
Obviously, only pendant groups which have not participated in a cyclisation reaction can split off in this manner. If this mechanism is correct, the TVA evidence suggests that there are a greater number of such unreacted groups in PMIK than remain in PMVK, that is the cyclisation process goes to a greater extent of conversion in PMVK than in PMIK.

The Origin of the "Cold Ring Fraction".

The formation of the cold-ring fraction roughly parallels the production of non condensable material in both polymers, suggesting that a fragmentation of the chain may follow the elimination of pendant groups, as indicated in the above reaction scheme.

TG shows that the polymeric residue resulting from water elimination, is unstable in the case of both polymers, weight loss extending to approximately 95% in each case. It has already been suggested that unreacted pendant groups are a possible source of this instability. However, another site of chain scission may be the bridging methylene group between "incompatible" ring formations such as E and F. (page 148). This process can be visualised as involving the breaking of the bond between the

methylene group and the adjacent ring structure, possibly accompanied by hydrogen transfer. Scission of this bond would lead to the formation of the cold-ring fraction, without concurrent production of non condensable material:-



(F).

Presumably, this is the more important mode of chain scission in PMVK.

Comparison of the TGA and TVA traces for PMVK reveals an interesting feature. Approximately 50% of the total weight loss from PMVK samples occurs above 370°C, yet above this temperature the Pirani traces suggest that volatilisation is almost complete, although the cold-ring fraction is being produced. Thus the formation of this product fraction registers as a weight loss,

but does not appear as a Pirani output, owing to the cold-ring fraction being largely involatile at room temperature.

Relative Extents of Cyclisation in PMVK and PMIK.

Evidence exists to suggest that the cyclisation reaction in PMIK goes to a lesser extent of conversion than in PMVK:-

(a) As mentioned previously, Marvel [57] showed that the percentage of the original oxygen content eliminated as water from PMIK was less than that evolved from PMVK, under similar conditions.

(b) The greater amount of carbon monoxide and methane evolved from PMIK than from the same weight of PMVK can be interpreted as being due to the presence of a greater number of unreacted pendant groups in PMIK than in PMVK.

(c) Cooper and Catterall [64] have observed that in the presence of base, PMIK colours (as a result of base catalysed cyclisation) more slowly than PMVK.

A possible explanation of these points can be made in terms of the well established principles of conformational analysis [65].

It has been established that cyclohexane ring systems will adopt that conformation which minimises unfavourable steric interactions between substituents attached to the six-membered ring. In particular, where bulky substituents occupy positions 1-3

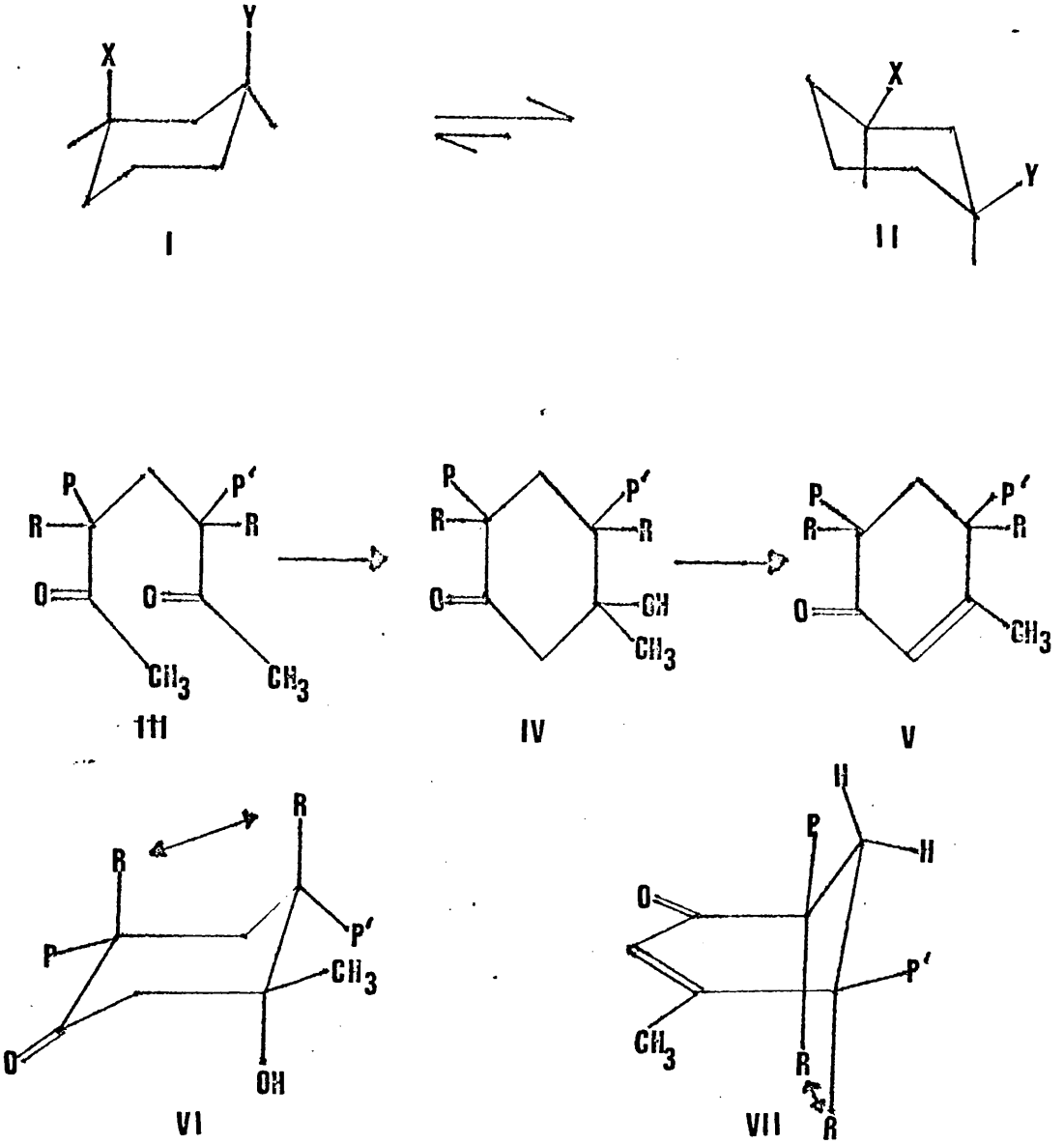
relative to one another on the ring, the conformation adopted will be such as to minimise "diaxial" interactions. Thus, in figure (5,13) conformation I will be of higher energy than II. The energy separation between the alternative conformations will be a function of the size of the groups X and Y.

The ring closure reactions in PMVK and PMIK probably proceed via the 2-hydroxy cyclohexanone IV, which eliminates water, giving the cyclohexene-one, V [18].

The conformation adopted by IV is probably VI. P and P', being portions of the polymer chain, are extremely bulky, and are therefore forced to adopt the equatorial-equatorial positions shown. This forces the two R groups into 1-3 dioxial positions. Clearly, where R = CH_3 (in PMIK) the interaction between the groups will be greater than for R = H (in PMVK). Thus the formation of the cyclohexanol is sterically hindered in PMIK. Similarly, there is interaction between the groups R in the cyclohexenone V, as indicated in VII. We would thus predict that the larger was group R, the slower would be the coloration reaction. The results of Cooper and Catterall [64] suggest that the reactivity towards base follows this prediction.

SUMMARY.

Under temperature programmed conditions, the effect of heat



FIGURE(5,13), Ring closure in PMVK and PMIK

on PMVK is to cause the splitting out of water from adjacent side groups by a random process, giving a fused ring system as the first formed product. As the temperature is raised, chain scission occurs, leading eventually to a total weight loss as great as 95%. This scission process appears to involve fission of bonds between adjacent ring structures, rather than breakdown of the rings themselves, and is accompanied by the production of small amounts of methane and carbon monoxide. The residue remaining above 500°C is stable, to temperatures greater than 800°C, and is presumably a form of carbon.

The thermal decomposition of PMIK, under the same conditions, is superficially similar, although the following differences in behaviour are apparent:-

(1) Monomer production occurs in PMIK, proceeding concurrently with the early stages of the coloration reaction. The yield of monomer is prevented from attaining 100% by the cyclisation process, since the formation of the six membered rings greatly reduces the kinetic chain length of depolymerisation.

(2) The large amount of methane and carbon monoxide evolved in the later stages of the decomposition of PMIK can be taken as an indication that cyclisation in this polymer is less efficient than in PMVK. A steric interpretation for this factor has been advanced.

CHAPTER SIX.

THE THERMAL DEGRADATION OF RANDOM COPOLYMERS OF METHYL METHACRYLATE WITH VINYL CHLORIDE.

The work described in this Chapter forms a part of a wider investigation, concerned with the thermal degradation of polymer blends, in particular, the poly (methyl methacrylate) (PMMA) - poly (vinyl chloride) (PVC) system.

In the study of mixed polymers the broad objective is to observe in what way, if any, the thermal degradation behaviour of a polymer molecule is changed by the presence of another polymer. In the study of copolymers, however, interest is taken in the effect on the thermal behaviour of a polymer, of the presence of foreign monomer units in the polymer chain. Clearly it is of interest to compare the two situations.

In this chapter discussion will be limited to discussing the degradation of the copolymers of MMA and VC. In a subsequent Chapter, experiments on PMMA - PVC mixtures will be described, and the behaviour of copolymers and mixtures will be compared.

It is convenient at this stage, therefore, to review briefly the state of knowledge regarding the degradation behaviour

of the parent homopolymers.

DECOMPOSITION OF PVC.

General Features.

PVC on heating, rapidly discolours, and liberates hydrogen chloride. It has been established that the colouration is caused by the formation of a polyene chain, A.

$$-CH_2-CHCl-CH_2-CHCl- \xrightarrow[-HCl]{} -CH=CH-CH=CH-$$

The elimination process is not random in nature since even at very low extents of dehydrochlorination, long polyene sequences are formed, and almost all of the chlorine is eventually eliminated as HCl. The process has therefore been termed a "Zipper" reaction.

At elevated temperatures, the polyene residue is believed to undergo rearrangement, associated with cross linking and the evolution of benzene and other hydrocarbons, the final product being an involatile, carbonaceous residue. This carbonisation process has been studied by several authors [78].

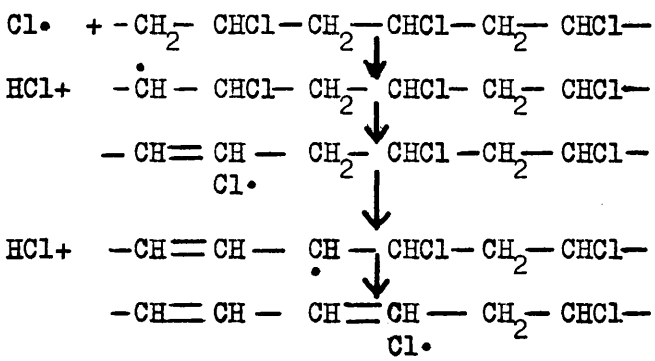
The intimate details of the mechanism of the dehydrochlorination of PVC have not yet been agreed upon. Various authors have suggested that the process occurs by a radical [13], ionic [11] or molecular [12] pathway, and evidence has been advanced to support each viewpoint. The major arguments for each case are summarised below:-

Radical Mechanism.

The radical mechanism, as proposed by Stromberg [13] is shown below:-

Initiation: PVC $\longrightarrow$ Cl•

Propagation:



Termination:

$$Cl\bullet + Cl\bullet \longrightarrow Cl_2 \qquad (a)$$

$$R_1\bullet + R_2\bullet \longrightarrow R_1 + R_2 \text{ or } R_1R_2 \qquad (b)$$

$$R\bullet + Cl\bullet \longrightarrow R\,Cl \qquad (c)$$

where R• = polymer radical, R = polymer molecule.

The evidence for this mechanism is circumstantial, rather than conclusive. Stromberg [13], assuming that the termination step was mainly (a), accounted for the 3/2 order which he observed. However, chlorine has never been detected in the volatile products (possibly owing to its great reactivity).

Radical species have been detected, in previously heated PVC, by ESR measurements conducted at room temperature [79]. However, carbonaceous residues, of the type formed in PVC degradation, have

the property of exhibiting ESR spectra due to unpaired electrons present in long polyene sequences, or aromatic rings formed during the carbonisation process. Certain combinations of pi-orbitals have the ability to undergo spontaneous homolytic scission, giving rise to a diradical. The unpaired electrons so formed can be accommodated in vacant, low energy, pi-orbitals. It is to the presence of such species, rather than intermediates in the dehydrochlorination reaction, that the ESR signals have been attributed [79].

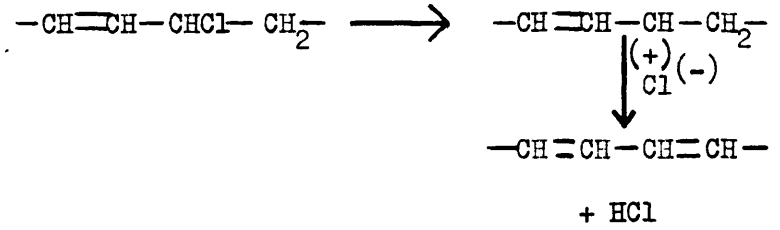
When radicals are produced in PVC by irradiation, they are known to cause liberation of HCl, to produce polyene sequences of the type produced thermally [80]. Also, the addition to PVC of free radical initiators, for example dicumyl peroxide, leads to increased rates of dehydrochlorination at 150°C in a nitrogen atmosphere [22]. Facts of this type prove that PVC can liberate HCl by a radical process, but do not prove that the dehydrochlorination, in the absence of such stimuli, involves radical intermediates. Obviously, it would be more conclusive to show that free radical scavengers inhibit the loss of HCl, but no successful experiments have yet been reported in this context.

A radical mechanism has been invoked to explain the accelerated rate of dehydrochlorination of PVC in oxygen, involving

the production of unstable hydroperoxides, which participate in a "chain branching" process. However, no free radical mechanism has yet been proposed which can satisfactorily account for the so-called autocatalytic effect in PVC degradation, in which HCl is believed to increase the rate of dehydrochlorination [71]. It should be pointed out, however, that catalysis by HCl has been refuted by some workers [81].

Ionic Mechanism.

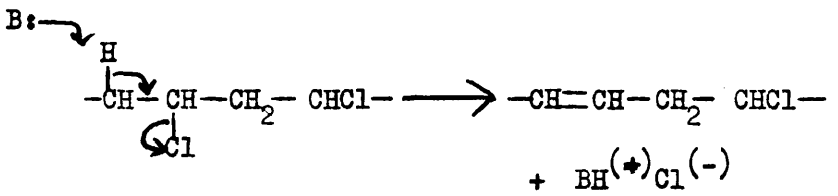
Marks et al [11] are among the most recent authors to suggest that PVC degrades by an ionic mechanism, involving the propagation step:



They base their argument on the nature of the reaction between PVC and stabilisers of the type R_2 Sn Y_2, which they believe proceeds by an ionic mechanism of the Friedel-Crafts type. They also point out that the dielectric constant of PVC at degradation temperatures may be sufficiently high to support the charge separation process necessary for ionic intermediates to be formed. The catalytic effect of HCl on the process is, they propose, a

result of the known ability of HCl to catalyse carbonium ion reactions.

In support of the ionic mechanism, it is known that nucleophilic reagents such as sodium methoxide, or benzyl trimethyl ammonium hydroxide, can cause loss of HCl from PVC, presumably by a mechanism such as that shown below [82]:-



Again, however, the evidence for the ionic mechanism is circumstantial rather than conclusive, and although ionic intermediates may indeed be present when PVC is heated in the presence of organo-tin stabilisers, or nucleophilic species, this does not prove that an ionic mechanism operates in the absence of such additives. It is certainly true, however, that most commercial stabilisers for PVC are not noted for their participation in radical reactions.

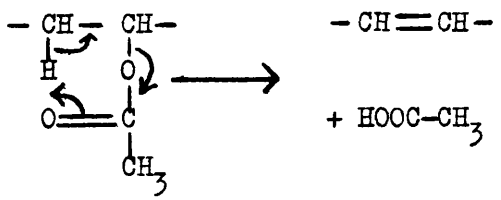
Molecular Mechanism.

According to the molecular mechanism for dehydrochlorination, HCl is liberated from the polymer by a concerted mechanism, without the intermediate formation of either radical or ionic species.

The initiation step in this process is visualised as being the loss of HCl from a labile centre in the molecule (at a chain end, a branching point, or oxidised structure). Once a molecule of HCl is lost from the chain, then allylic activation of the neighbouring hydrogen promotes the loss of a further molecule of HCl, giving rise to the observed "Zipper" characteristic of the process.

$$-CH{=}CH-CH_2-CHCl- \xrightarrow{-HCl} -CH{=}CH-CH{=}CH-$$

The mechanism proposed is similar to that which has been proposed in the case of poly (vinyl acetate) decomposition [83]. However, in the case of the latter, a six membered transition state can be visualised:-



There is no such driving force for the dehydrochlorination of PVC.

In essence, a molecular mechanism is equivalent to an ionic or radical process in which $Cl^{(-)}$ or Cl• does not become fully detached from the PVC molecule, and tends to attack the

neighbouring hydrogen preferentially, rather than migrating to another polymer chain.

Point of Initiation of the Dehydrochlorination.

PVC, in common with many other polymers, is considerably less stable than would be expected from model compounds. Presumably, therefore, PVC molecules contain labile centres at which the dehydrochlorination reaction is initiated. The manner in which these labile centres break down will determine the subsequent mechanism of degradation, i.e. if radicals are formed in the initiation step, the subsequent dehydrochlorination reaction will be a radical process. However, no agreement exists on the point of initiation, although several possibilities have been advanced.

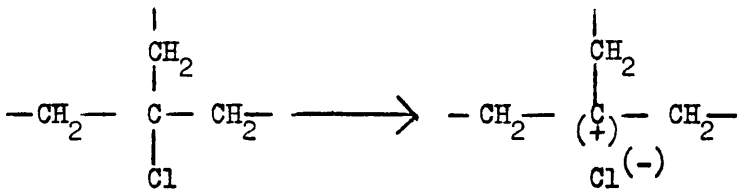
Chain Ends.

It has been shown [81] that low molecular weight polymer discolours more rapidly than high molecular weight fractions, which is strong evidence that molecular chain ends are a source of instability. There is some evidence to suggest [13,84] that varying the type of initiator system used to make the polymer changes the thermal stability of the final material, indicating that initiator fragments, at the end of the polymer molecule, may be the site of initiation. However, the source of instability

may be unsaturated end groups, formed by termination or transfer reactions, rather than the catalyst residues.

Branch Points.

It is known that PVC has a tendency to form branch points in the course of polymerisation. These have been proposed as a possible site of initiation for the ionic mechanism, since they are a site of tertiary chlorine atoms, which are more likely to be lost to give a tertiary carbonium ion [11]:-



Oxidised Structures.

Geddes [22] has shown that hydroperoxide groups deliberately introduced into PVC are a source of instability. The same author points out, however, that no positive proof exists to suggest that such groups are formed under normal conditions in PVC.

Clearly, PVC can be induced to lose HCl by radical or ionic pathways. The question remains unanswered as to how the polymer degrades in the absence of radical or ion promoting reagents. The increasing number of publications on this topic in recent years is evidence of the interest still being devoted to the controversy.

DECOMPOSITION OF PMMA.

By contrast to the confused state of knowledge of PVC degradation, the major features of the thermal decomposition of PMMA have been fully elucidated.

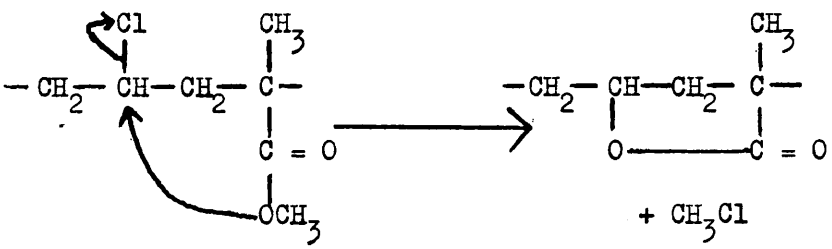
It has been established by Grassie [3], and later workers [5,6], that the decomposition of this polymer is a radical chain depolymerisation process, occurring in two stages. The first, lower temperature reaction, consists of unzipping to monomer of radicals produced exclusively at unsaturated end structures (if such are present in the polymer). At higher temperatures (above 300°C), the main backbone of the polymer becomes unstable, and random scission of carbon-carbon bonds occurs producing radicals which again unzip to monomer as the exclusive product. In both processes, the zip length of depolymerisation is very large, and transfer reactions are believed to be unimportant. However, McNeill [6] has shown that the presence of small amounts of a second monomer, copolymerised into the PMMA chain can reduce considerably the efficiency of monomer production, i.e. reduce the kinetic chain length of depolymerisation.

PREVIOUS WORK ON THE COPOLYMERS.

Barlow, Lehrle and Robb [25] made a study of the thermal decomposition of random and block copolymers of MMA and VC, using

pyrolysis - gas chromatography. It was noted that the random copolymers were less stable than block copolymers, or a blend of the parent homopolymers. In explanation it was suggested that the methyl methacrylate unit adjacent to a vinyl chloride unit was capable of initiating the loss of hydrogen chloride, via a ring transition state.

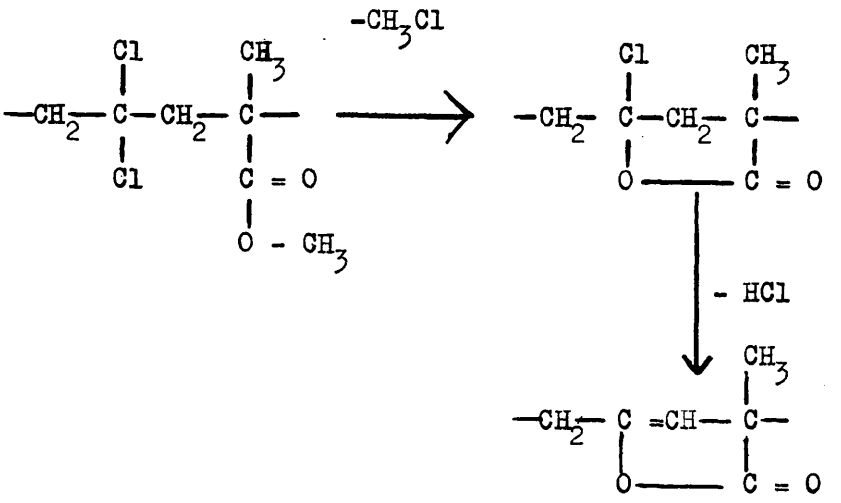
Zutty and Welch [85] studied the thermal behaviour of copolymers of MMA and VC, and showed that at temperatures as low as 150° the copolymers liberated methyl chloride almost quantitatively by a lactonisation reaction:



Under these conditions, no chain scission took place, and cross linking was absent, confirming that the process was intramolecular rather than intermolecular.

The reaction was shown to be general for polymers containing alpha - substituted gamma - haloester groups in their backbone. Thus Burnett, Haldon and Hay [24] showed that a similar process occurred in MMA - vinylidene chloride copolymers, although lactonisation could be followed by elimination of a

further chlorine atom as HCl:-



The work of Barlow, Lehrle and Robb, Zutty and Welch, and Burnett, Haldon and Hay indicated clearly that lactonisation occurred more readily than dehydrochlorination. However it was not established in what way the lactone rings so formed affected the upper temperature stability of the polymer chain, i.e. whether the lactones were a source of instability in the polymer molecule.

STRUCTURE OF POLYMERS.

Five VC-MMA copolymers were prepared by A. Gunnee (BSc. student), the details of preparation being given in Appendix 1. The mole fraction of VC in the polymers ranged from 0.022 to 0.309, calculated on the basis of the reactivity ratios VC 0, MMA 12.5 [86]. Assuming these reactivity ratios to be correct, the following

points can be made concerning the composition of the final product:-

(1) Polymers of low VC content will tend to consist of single VC units flanked by long strings of MMA units.

(2) As the VC content increases, there will be a greater tendency towards alternation, and a structure of the type (A) shown below will obtain:-

M-M-M-V-M-V-M-M-M-M-V-M-M

(A)

where M = methyl methacrylate and V = vinyl chloride unit.

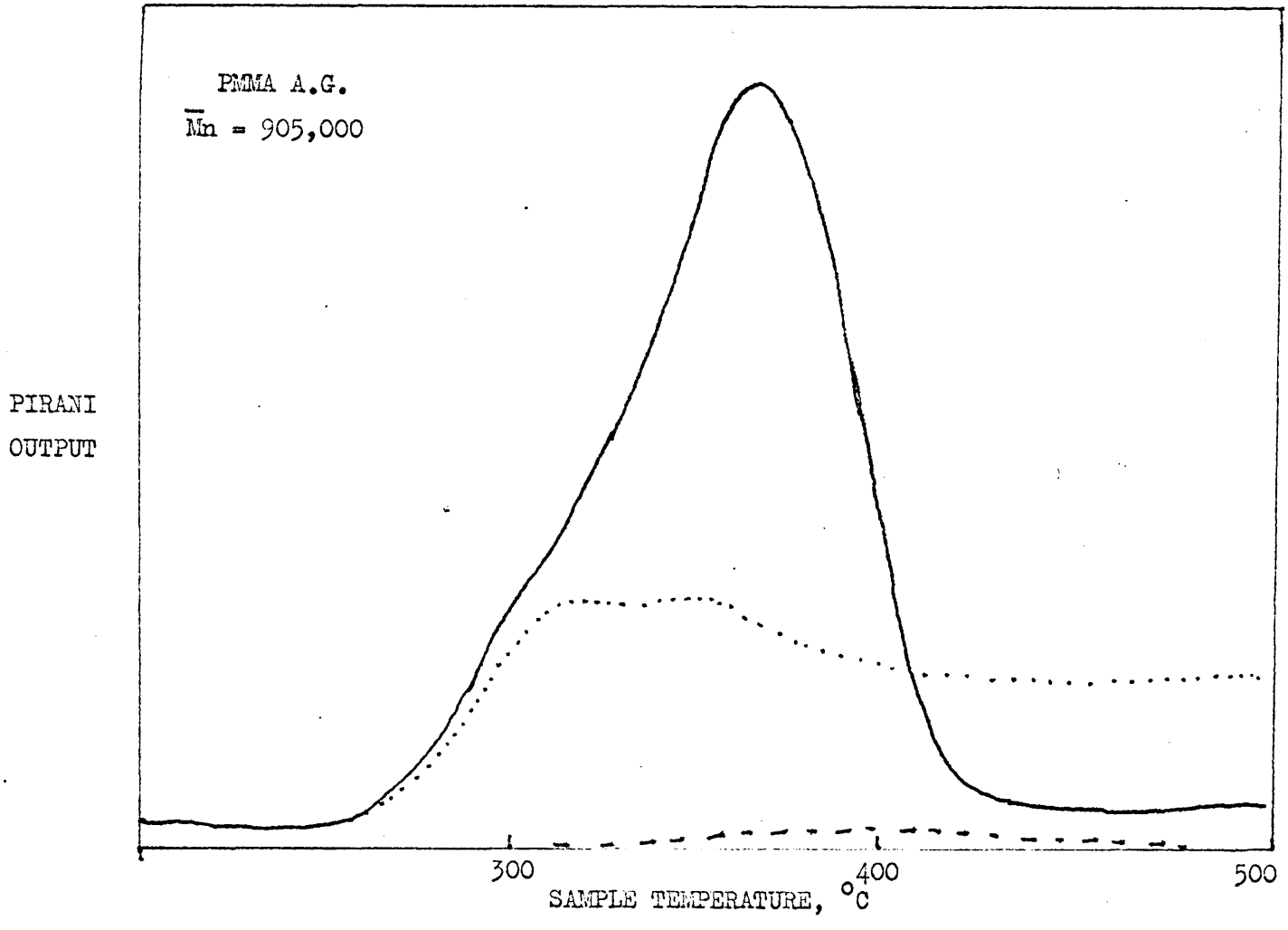
However, the reactivity ratios suggest once a vinyl chloride unit has added to the growing polymer chain, the next unit to add to the chain will invariably be methyl methacrylate, and not another vinyl chloride unit. This means that structures of type B, containing strings of VC units should not arise:-

M-M-V-V-V-M-M-M-M-M-M

(B)

TVA THERMOGRAMS.

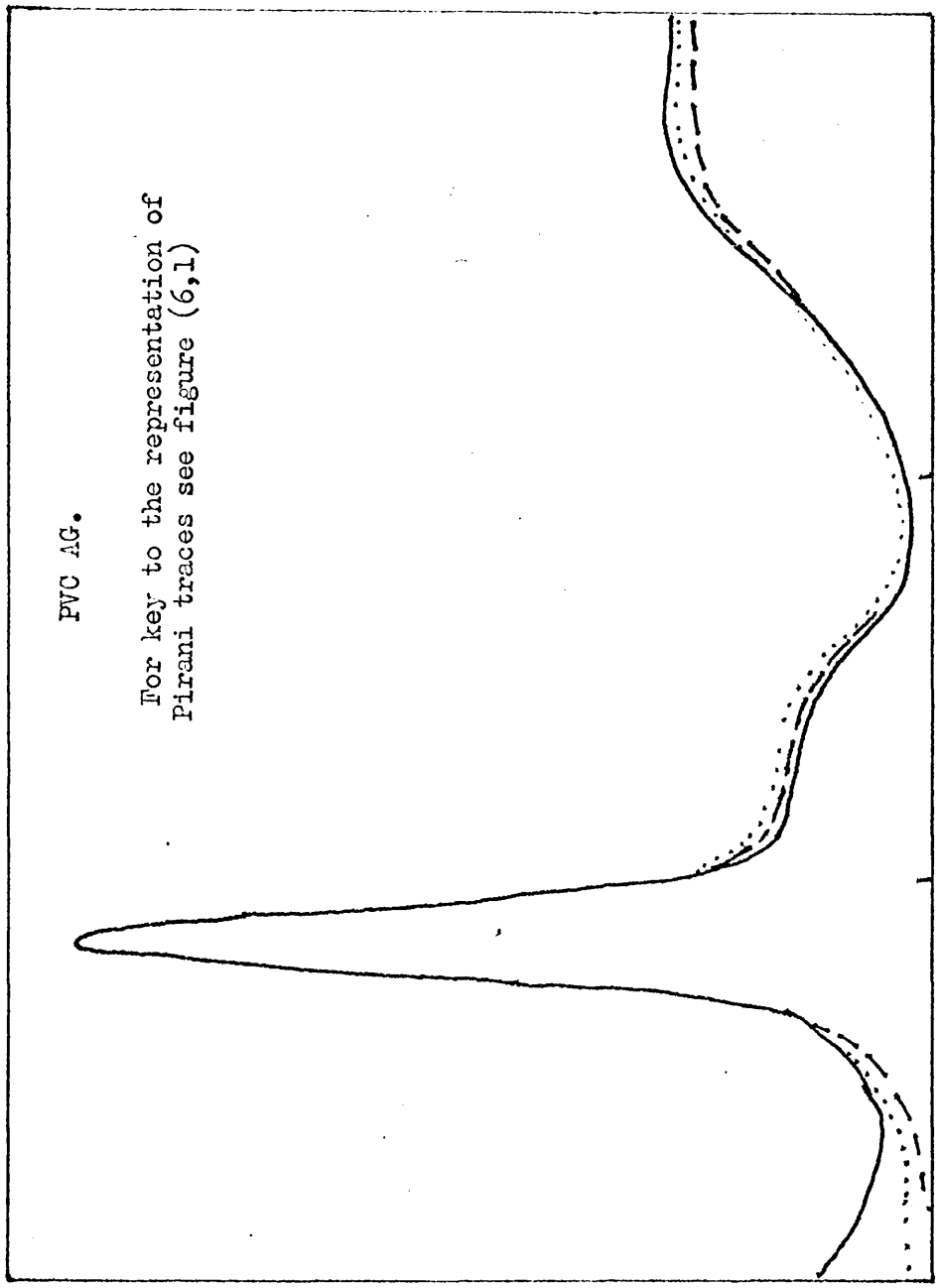
DCTVA thermograms were obtained at 10^{o}/min, for 50 mg samples of the copolymers, and also for a PMMA sample and a PVC sample prepared under the same conditions as the copolymers (see Appendix 1), and these are shown in figures (6,1) to (6,7). The PMMA and



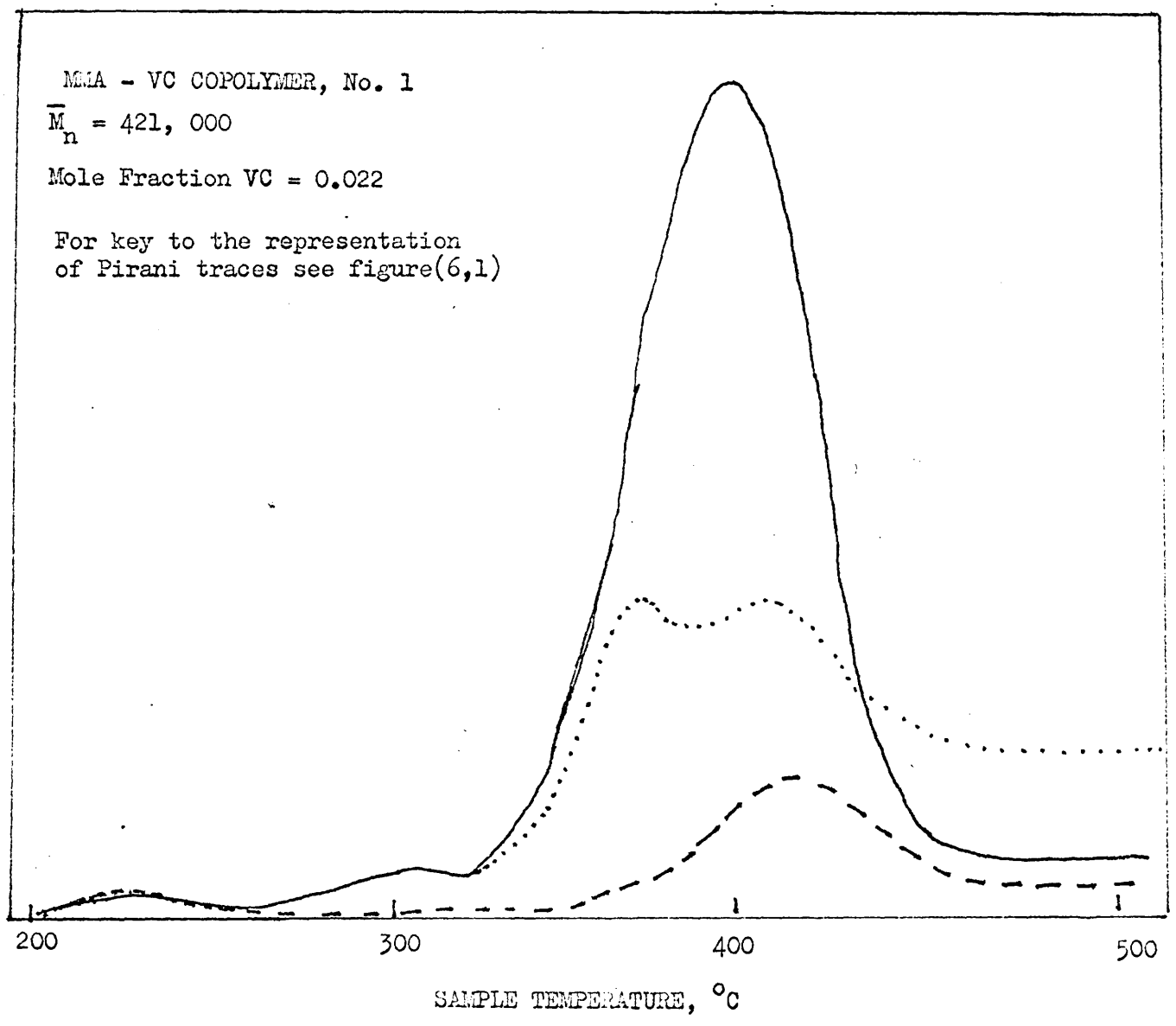
FIGURE(6,1), DC-TVA Thermogram for PMMA AG., at 10°/min., (50mg.),sample as fine powder

– – – – – gauge after trap at -100°C, ... gauge after trap at -75°C

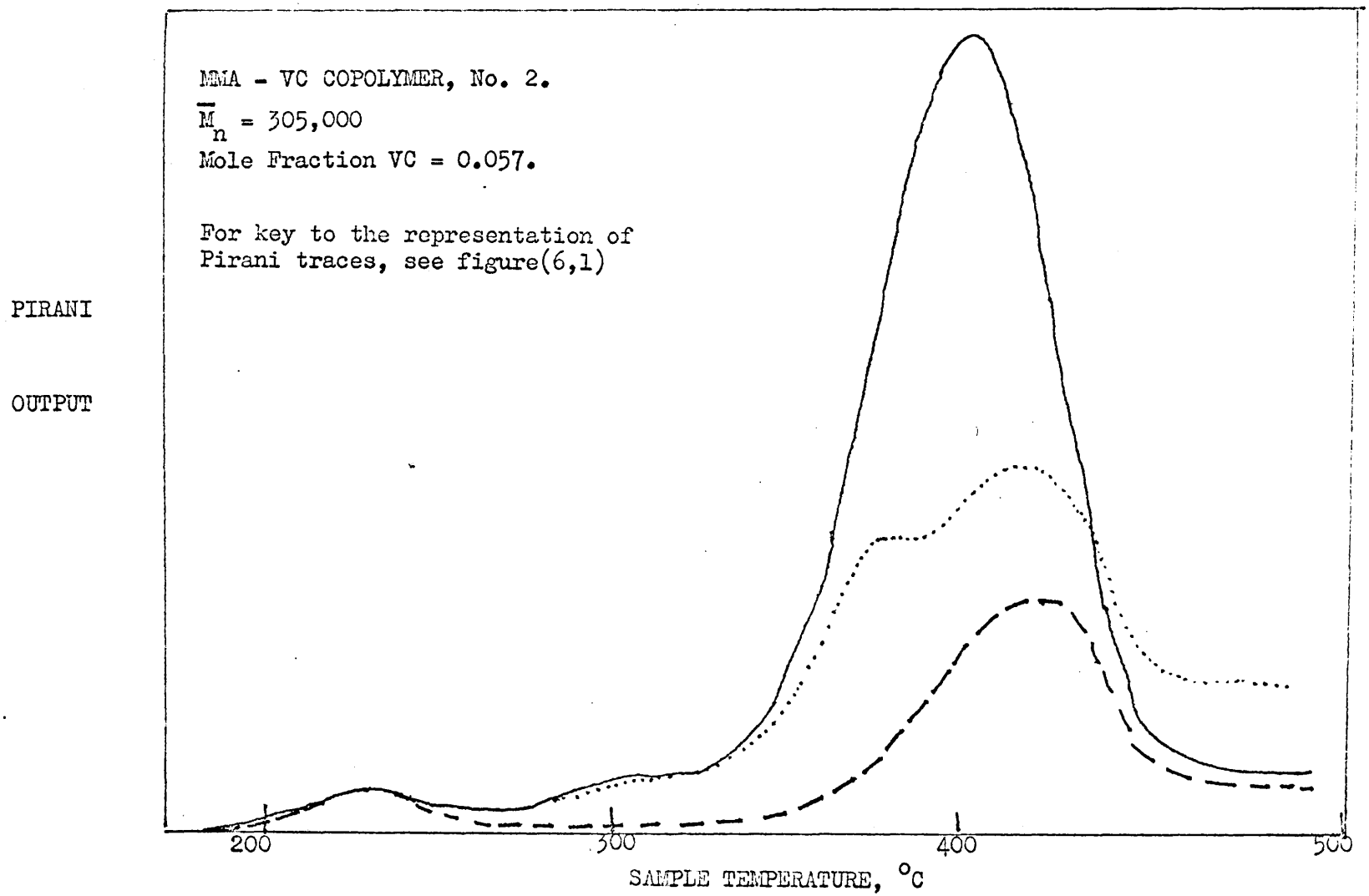
——————— gauge after traps at 0and -45°C



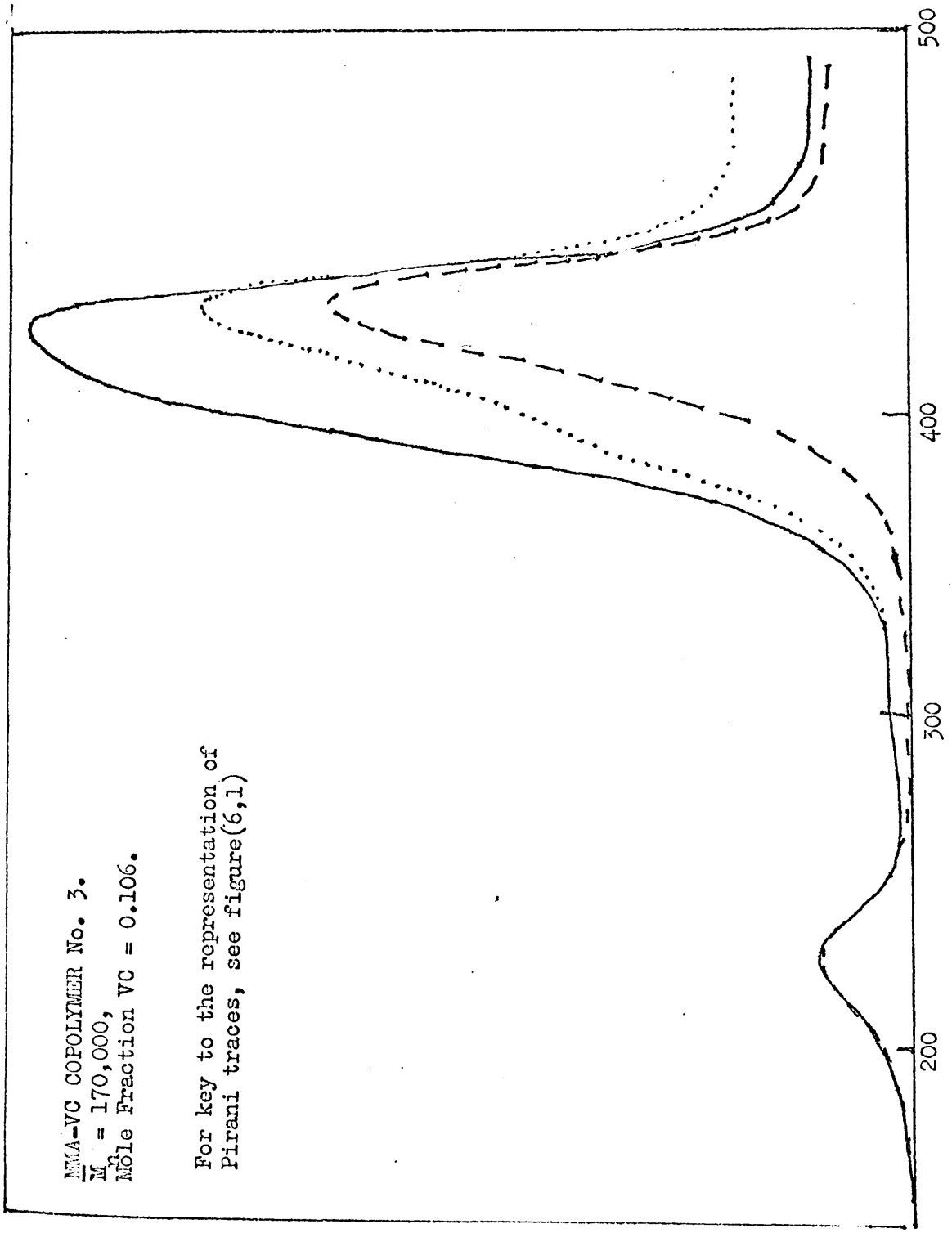
FIGURE(6,2), DC-TVA thermogram for PVC AG (50mg), at 10°/min., sample as thin slices



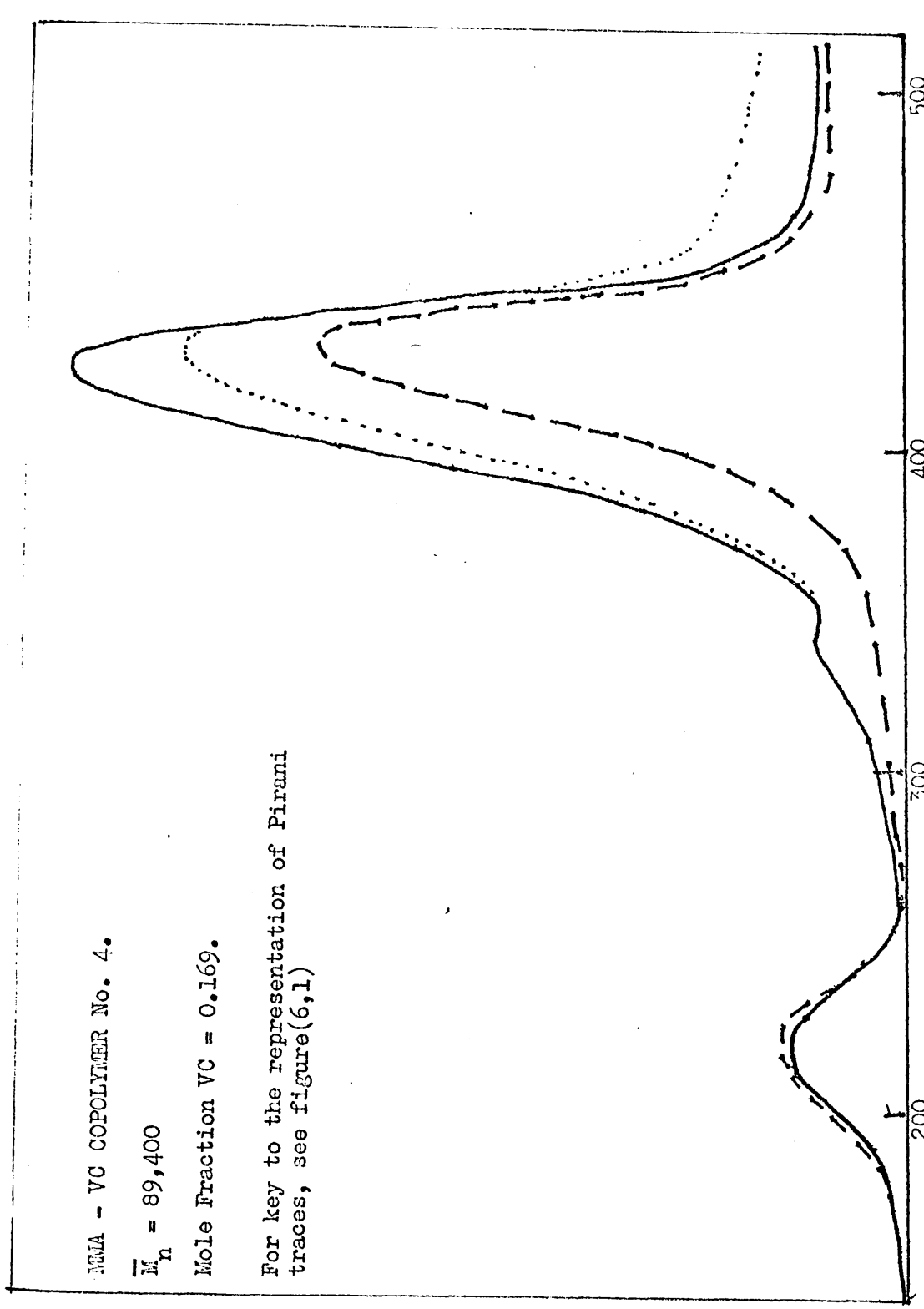
FIGURE(6,3), DC-TVA thermogram for MMA-VC copolymer No.1 (50mg.), at 10°/min., sample as a fine powder.



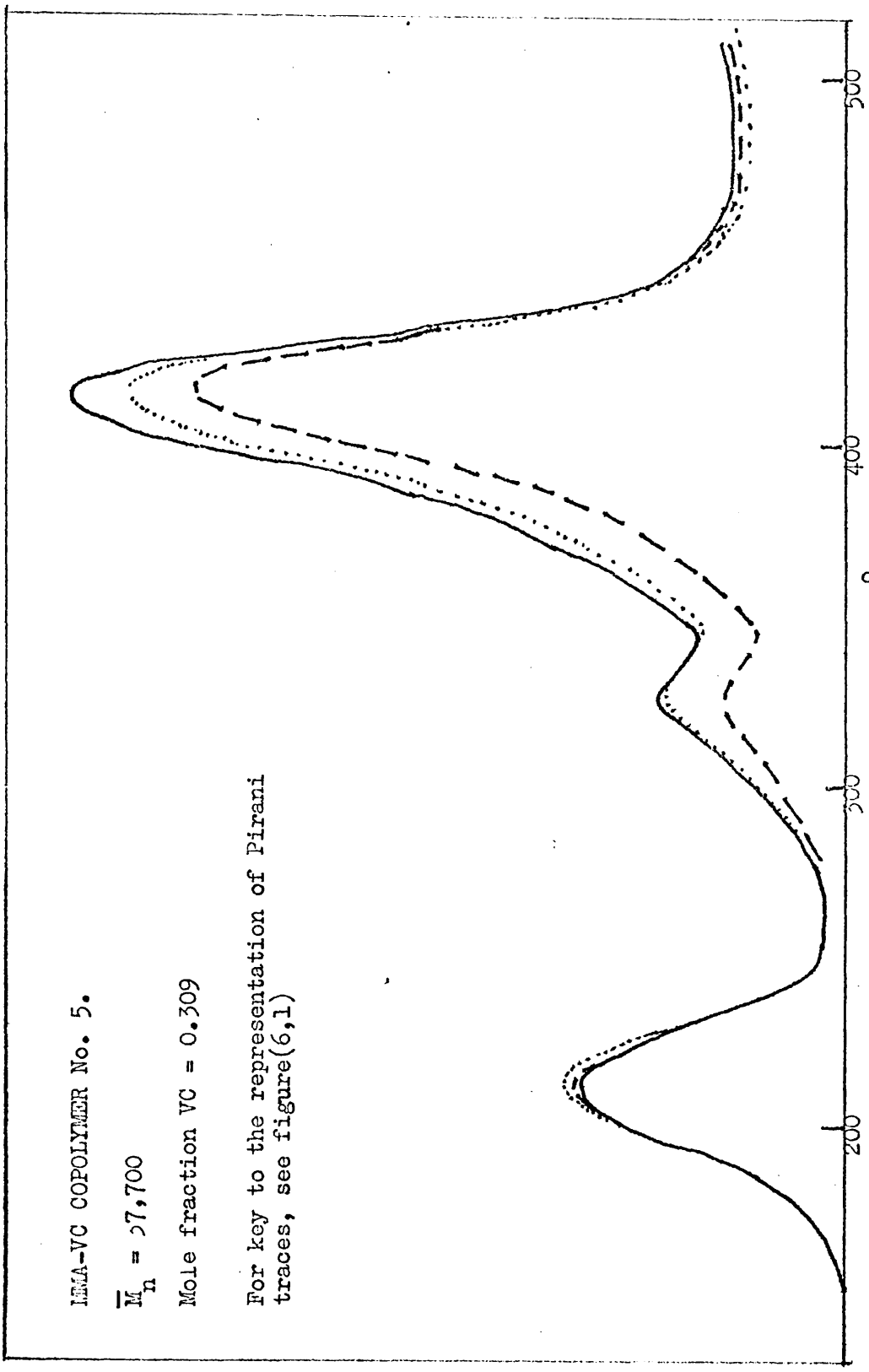
FIGURE(6,4), DC-TVA thermogram for the degradation of MMA-VC copolymer No. 2 (50mg), at 10°/min., sample as a fine powder.



FIGURE(6,5), DC-TVA thermogram for MMA-VC Copolymer No. 3 (50mg), at 10°/min., sample as a fine powder.



FIGURE(6,6), DC-TVA thermogram for MMA-VC Copolymer No.4(50mg), at 10°/min., sample as a fine powder.



FIGURE(6,7), DC-TVA thermogram for MMA - VC Copolymer No 5, (50mg), at 10°/min., sample as fine powder.

the copolymers were in the form of fine powders, although the PVC sample, which was soft and rubbery, was degraded as thin slices. Trap temperatures were, as usual, 0°, - 45°, - 75° and 100°C respectively.

INTERPRETATION OF THERMOGRAMS.

(a) **PMMA.**

The thermogram consists of a main peak at 370°C, with a small shoulder at 290° - 300°C. The - 75°C trace shows the typical behaviour of methyl methacrylate, slowly distilling to the trap at liquid nitrogen temperature. The shoulder on the main peak can be ascribed to monomer production initiated exclusively at unsaturated end structures, while the main peak represents monomer production following random scission in the main chain. As would be expected, the amount of material not condensed at - 100°C, is negligible. Volatilisation below 200°C is due to solvent elimination as the polymer softens.

(b) **PVC.**

As can be seen, almost all of the degradation products from this polymer are not condensed at - 100°C. The peak at 275°C, with a long "plateau" extending 350°C is due to HCl production, the "plateau" being a sample form effect (see Chapter 3, pages 102-105). Above 400°C, the residue from the dehydrochlorination becomes

unstable, and begins to acquire its aromatic character, benzene being the major product in this temperature range.

(c) Copolymers.

The thermograms for the copolymers progressively change in character as the VC content increases. The noticeable trends can be summarised:-

(a) The first peak in the copolymer thermograms, consisting of material which is not condensed at - 100°C, increases in height with increasing VC content, and represents a reaction which is not present in either homopolymer, since the Tmax for this peak (215 - 225°) is much earlier than the peaks in the PMMA or PVC thermograms.

(b) By contrast, the largest degradation peak for the copolymers comes later (405° to 425°C) than the main degradation peaks for PMMA or PVC. As the VC content increases, this peak is associated with the production of an increasing amount of material which is not condensed at - 100°C. In copolymers of low VC content, however, the peak is clearly associated with the production of methyl methacrylate, the presence of which is indicated by the - 75°C trace.

(c) A peak at 305°C, evident in copolymers of low VC content, and associated with the production of condensable material,

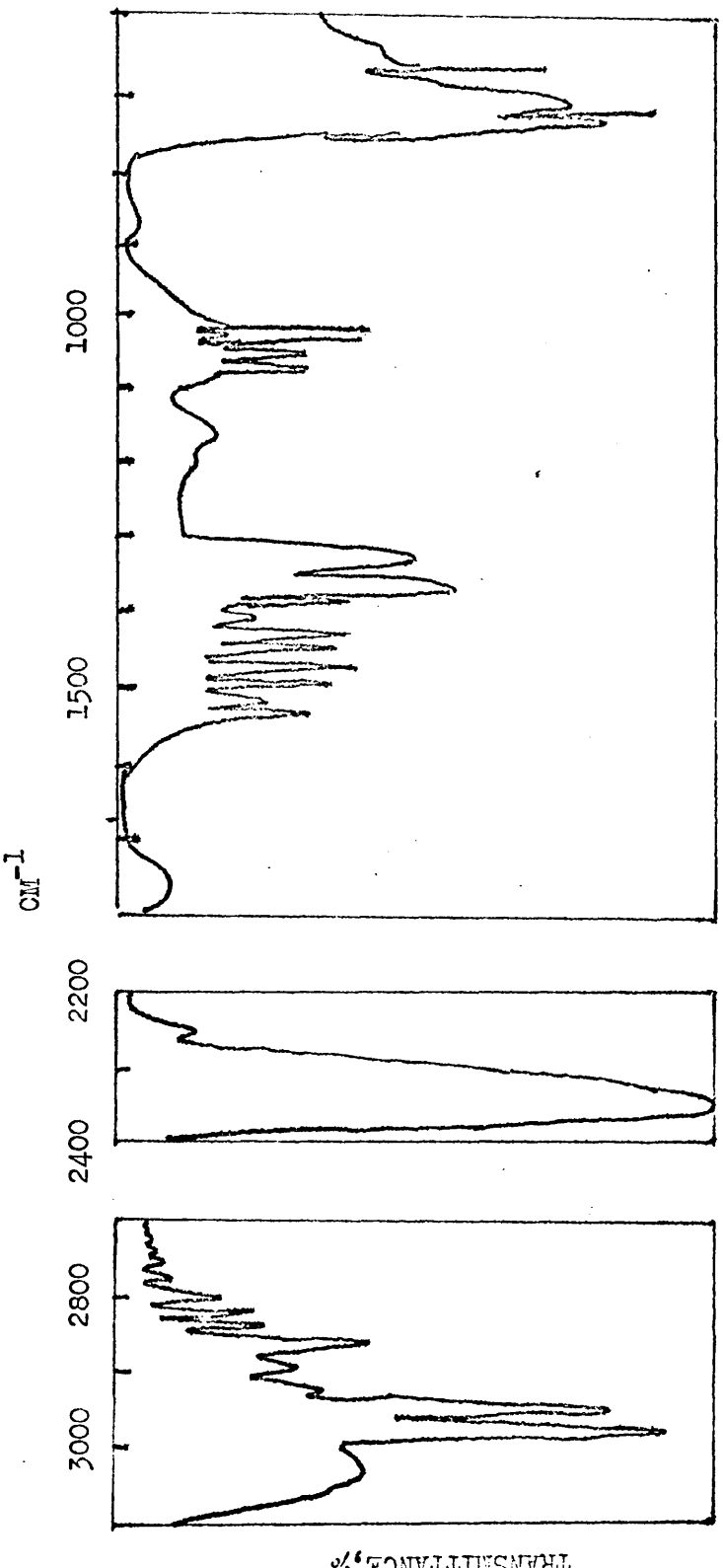
slowly disappears with increasing VC content and is replaced by a peak at 335° in copolymers of larger VC content, which is associated with the production of non-condensable material.

PRODUCT ANALYSIS.

The nature of those products non-condensable at - 75°C but condensable in liquid nitrogen was investigated by infra-red gas cell analysis. The spectrum of the products from copolymer 4 is shown in figure (6,8).

Peaks at 2950 and 2980 cm^{-1}, and bands at 1400-1500 and 700-750 cm^{-1} are characteristic of methyl chloride. The characteristic band spectrum of hydrogen chloride is evident from 2700 to 3100 cm^{-1}. Strong peaks at 2340 and 3700 cm^{-1} are indicative of carbon dioxide. Small peaks at 1750 and 1170 cm^{-1} are probably due to the small amount of methyl methacrylate evolved from this copolymer.

A sample of copolymer 4 was heated at 10°/min to a temperature of 260°C. The residue was then isolated and an infra-red spectrum taken. This was compared with the spectrum of the original copolymer. The appearance of a new peak at 1770 cm^{-1} can be ascribed to the formation of lactone rings, as reported by Zutty and Welch (85).



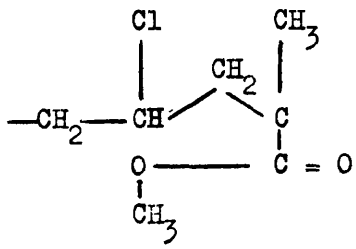
FIGURE(6,8), Infra-red spectrum(Gas cell) of those products of degradation of a MMA - VC copolymer which are volatile at -75°C, but condensable in liqud nitrogen.

DISCUSSION.

Lactonisation Reaction.

The increase in the first peak of the copolymer thermograms with increasing VC content is as would be expected, being associated with an increased yield of methyl chloride.

It is somewhat surprising that the lactonisation should occur at temperatures below those supporting HCl production from PVC. In the case of PVC degradation, the rapidity of HCl loss is caused by allylic activation. In MMA - VC copolymers, the rapidity of lactonisation is almost certainly due to the favourable relative positions of the reactive groups on the polymer chain:-



Effect of Lactone Rings on stability.

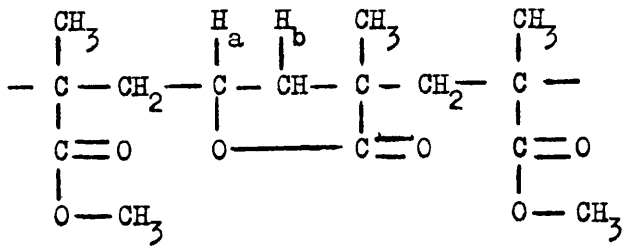
The infra-red spectrum of the gaseous degradation products clearly shows that carbon dioxide is an important product. Examination of the TVA thermograms of the copolymers shows that with increasing VC content, the - 100°C peak, with a Tmax at 410° to 430°C, increases. Most probably, this is due to carbon

dioxide production from decomposition of lactone rings, or MMA units which have not been removed from the polymer chain by the depolymerisation reaction.

The presence of the lactone rings also causes the peak corresponding to monomer production to be displaced to higher temperatures than in a pure sample of PMMA (from approx. 370°C in the homopolymer to approx. 420° in copolymers), possibly because the lactone rings act as "blocking" units towards the depolymerisation reaction, that is reduce the kinetic chain length of depolymerisation.

Lactone rings might reduce the zip length in two ways, either by increasing hydrogen transfer reactions, or by acting as sites which are incapable of continuing the unzipping process.

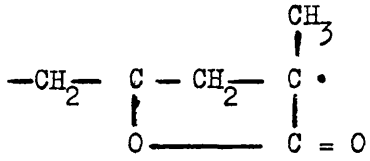
In the first instance, it can be seen that the lactone ring contains both tertiary and secondary hydrogen atoms, a and b respectively:-



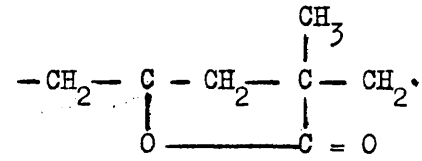
These hydrogen atoms might be more susceptible to abstraction by a polymer radical than the hydrogens in PMMA, since they are

less sheltered sterically.

The alternative explanation is that radicals of type 1 or 2, shown below, formed by unzipping the chain as far as a lactone unit, are incapable of permitting the unzipping reaction to pass through them:-



(1)



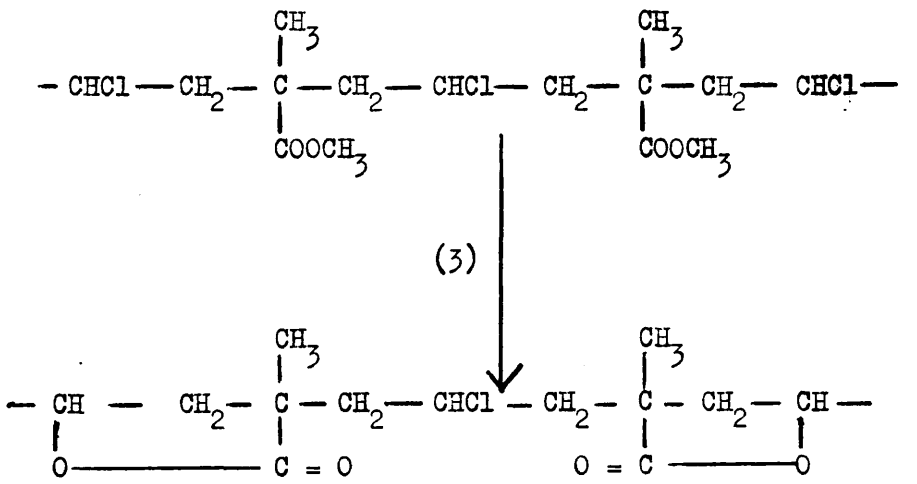
(2)

A feature of the thermograms already mentioned is the disappearance, with increasing VC content, of the small peak at 305°C, due to the production of condensable material, and the appearance of a peak at approximately 330°C, in which both condensable and non condensable material are simultaneously produced.

The former peak, which is only present in copolymers 1 to 3, is almost certainly due to the production of monomer, the depolymerisation being initiated at unsaturated end structures. The peak probably disappears because the kinetic chain length of depolymerisation is reduced, owing to the blocking action of the lactone rings.

It is more difficult to explain the appearance of the new

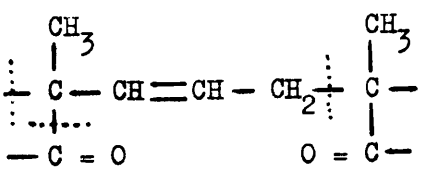
peak in copolymers 3 and 4. It should be noted, however, that as the VC content is increased, the copolymer structure changes. In copolymers of low VC content, the chains consist of isolated VC units, flanked by long sequences of MMA units. As the VC content increases, there will be a greater tendency towards alternation. Consider a chain sequence of type (3) below:-



(3)

(4)

It is possible that some VC units may be unable to undergo lactonisation, since the neighbouring methyl methacrylate residue will react in a purely random way. Most probably, such a unit will eliminate HCl, giving a main chain double bond:-



(5)

It might be supposed that the additional peak in copolymers 3 and 4 is associated with elimination of HCl from such units. If this were so, the peak would be wholly non-condensable at - 100°C, which is clearly not the case. However, it may be that units such as (5) once formed, constitute weak points in the polymer chain, at which depolymerisation might be initiated, by cleavage of the bonds shown. McNeill [6] has shown, by study of MMA - phenylacetylene copolymers, that main-chain unsaturation is a source of instability in PMMA.

It is possible, therefore, that the condensable fraction of this peak is due to methyl methacrylate produced by depolymerisation of the polymer chain, the reaction being initiated at unsaturated linkages such as (5).

SUMMARY.

The thermal decomposition behaviour of copolymers of MMA and VC shows an interesting gradation with increasing VC content:-

(a) The copolymers are less stable than either homopolymer, undergoing an intramolecular lactonisation reaction, and liberating methyl chloride.

(b) The residue so produced is somewhat more stable than PMMA, since the lactone rings act as blocking units towards the depolymerisation reaction.

(c) The copolymers liberate an increasing amount of non condensable material, in the later stages of decomposition, as the vinyl chloride content is raised. The yields of methyl methacrylate from the copolymers fall correspondingly, as a result of the presence of the lactone rings.

(d) The appearance of a small peak in the thermograms of copolymers of higher VC content has been attributed to the formation of main chain double bonds at vinyl chloride units which are incapable of lactonisation, and the breakdown of such units to yield monomer.

CHAPTER SEVEN.

THERMAL DEGRADATION OF POLY (VINYL-CHLORIDE) - POLY (METHYL METHACRYLATE) MIXTURES.

INTRODUCTION.

In the main, studies of polymer degradation have been limited to investigation of the thermal decomposition of homopolymers, and to some copolymer systems. In recent years, however, increasing use has been made of composite materials, in an attempt to obtain a system having the physical properties of both components. For example, the impact strength of polystyrene is improved considerably when the polymer is blended with small amounts of natural rubber.

Considerable interest has therefore been taken in the physical properties of polymer blends, although the chemical properties of such systems have not been the subject of much study.

It is well known that the decomposition behaviour of a polymer molecule can be modified considerably by the presence of a second, foreign monomer unit in the chain. It is clearly of interest to the degradation chemist to observe whether or not polymers degrade differently in the presence of a second polymer.

Previous Work on Polymer Mixtures.

Probably the most significant study of the degradation of

polymer mixtures is that of Richards and Salter [87]. These authors found that monomer yields, as measured by GLC, from polystyrene samples, increased when the polymer was degraded in the presence of poly (alpha-methyl styrene). The latter polymer is known to be less stable than polystyrene, depolymerising almost quantitatively to monomer. The increased styrene yield indicates that radicals from this polymer are capable of initiating degradation in polystyrene, probably by abstracting hydrogen from the polymer chain.

Mizutani [88] has also presented evidence to suggest that the degradation of polypropylene is accelerated by the presence of other vinyl polymers, such as polystyrene or poly (methyl methacrylate). In this case, the vinyl polymers were also incorporated into the polypropylene chain, forming block and graft copolymers, presumably by a mechanism involving attack by a vinyl polymer radical on the polypropylene chain.

The oxidative thermal degradation of blends of polyacrylonitrile and acetyl cellulose has been studied by Vasile [89]. It was found that the energy of activation for the decomposition of the polymer blends was a function of the composition of the blend, and differed considerably from the value obtained by extrapolation of the energy values of the two components, indicating that some form of interaction was occurring.

Zutty and Welch [85], as part of their investigation of MMA - VC copolymers, studied the decomposition of PMMA - PVC blends. They found that small quantities of methyl chloride were evolved from the mixed system, but did not investigate further, or suggest a mechanism for the process.

As mentioned in Chapter Six, Barlow, Lehrle and Robb [25] noted that blends of PMMA and PVC were more stable than random copolymers of MMA and VC.

Purpose of this Investigation.

Results such as those described above clearly indicate that the degradation behaviour of a polymer molecule can be influenced considerably by the presence of a second polymer.

As previously stated (in Chapter Six) the mechanism of dehydrochlorination of PVC has not been clearly established. If, as some authors believe, the reaction involves radical intermediates, then the presence of these might be revealed when the PVC is degraded in the presence of a second polymer molecule. It was for this reason that the study described in this chapter was carried out.

STRUCTURE OF POLYMER BLENDS.

Nature of Incompatibility.

Studies of any mixed polymer system are complicated by the so-called incompatibility of unlike macromolecules. For example,

when unlike polymers are present in a common solvent, above a limiting total concentration, the solution will slowly separate into two layers, with a clearly defined phase boundary between them. Analysis of the two layers shows that one polymer has concentrated in the upper layer, while the other polymer is predominantly in the lower layer. The studies of Dobry and Boyer-Kawenoki [90] showed that this behaviour is typical of systems containing two polymers, and compatibility is the exception, rather than the rule.

The phenomenon of incompatibility is also exhibited in the solid phase. When attempts are made to achieve a uniform dispersion of one polymer in another by milling the two components together, or evaporating to dryness a solution containing the two components, the resulting composite is usually opaque or hazy in appearance, owing to the heterogeneity of the mixed system. Indeed where a clear mixed polymer film is obtained, it is usually taken as a sign that the polymer pair is compatible [91].

Mixed polymer systems have been studied by a variety of techniques, in order to examine their internal structure. Microscopic techniques reveal that at best, incompatible polymer pairs when milled, extruded or precipitated together, give rise to a system which consists of two phases, corresponding to the two polymers.

While one component will tend to form a continuous phase, the other will separate into micelles, of dimensions 1-15 x 10^{-4}cm. [92], which form a disperse phase in the continuous matrix of the first polymer. The intimacy of contact between the unlike molecules is thus much less than would be achieved by completely random mixing. In short, unlike polymer molecules have a low entropy of mixing.

Factors Affecting Compatibility.

(a) Nature of polymers.

Polymers are incompatible when the intermolecular forces between like molecules are greater than the forces between unlike polymer chains. It might be expected, therefore, that polymers of similar structure would tend to be compatible. Thus polystyrene and poly (O-methyl styrene) are compatible in solution [93]. Surprisingly however, blends of ortho- and para- methyl styrene polymers are not compatible [93], suggesting that the phenomenon of incompatibility is extremely sensitive to the structure of the polymer chains involved.

Concentration of polymers.

The phenomenon of phase separation in mixed solutions of unlike polymers is strongly dependant on the concentration of the solutes. Indeed, even where the polymers are incompatible, phase

separation does not occur until the concentration of the solution is approximately 40 mg./ml in each component, or greater [94].

Molecular Weight of Solutes.

Since the incompatibility of unlike polymers is a consequence of the molecular size, it is not unexpected that incompatibility has been shown to increase with increasing molecular weight of the solutes. Since genuine mixing of unlike polymers is prevented by the restriction of freedom imposed on the monomer units when they are bonded together in a polymer chain, the effect of increasing the molecular weight can be regarded as imposing an even greater restriction on the freedom of the monomer units to move relative to each other.

Temperature.

Increasing temperature is believed to reduce the incompatibility of the polymer pair, although the effect of this variable has not been fully investigated.

Consequences of Incompatibility.

Up to the present time, no way has been found to overcome the mutual incompatibility of unlike macromolecules. It must be accepted, therefore, that any polymer blend will not form a true mixture, and certainly not a solid solution. In the solid state, small regions, or micelles of one polymer will be distributed

throughout the matrix of the second polymer. Any chemical interaction which takes place between the components in such a system must either take place at phase boundaries, or involve the diffusion of a species formed in one phase into the second phase. Obviously in the latter case, the smaller the diffusing species, the more easily it will be able to diffuse through the polymer network. Thus Richards and Salter [87] believe that the species initiating breakdown of polystyrene, when it is present in a blend with poly (alpha methyl styrene), are low molecular weight radicals, arising from complete unzipping of the poly (alpha methyl styrene) chain, rather than first formed macromolecular radicals.

However, the interaction of a polymer radical with a polymer molecule of another type cannot be ruled out, since Mizutani [88] has shown that block and graft copolymers were formed in polypropylene - vinyl polymer blends.

POTENTIAL DIFFICULTIES IN THE STUDY OF MIXED SYSTEMS.

(a) Reproducibility of Sample Form.

The most serious consequence of the heterogeneity of polymer blends is the difficulty of achieving reproducible sample form, i.e. for a valid comparison to be made, one polymer should be dispersed to the same extent in the other polymer, on each occasion.

The ultimate test of any method adopted will be the reproducibility of the subsequent degradation experiments.

Richards and Salter [87] in the study of the polystyrene-poly (alpha methyl styrene) system, pyrolysed blends of the two components obtained by freeze drying a solution of the two polymers in benzene. Mizutani [88], when studying the effect on polypropylene of thermally degrading vinyl polymers, could not use such a technique, owing to the insolubility of polypropylene. The method of sample preparation adopted in this case was to evaporate to dryness, under continuous stirring, a slurry made of polypropylene in a solution of the second polymer, or to precipitate the slurry in methanol.

In the work described in this Chapter, it was decided that neither of these approaches was suitable. As stated in Chapter 3, the TVA thermogram of PVC is strongly dependent on the sample form employed. As with powdered samples, freeze-dried samples tend to give thermograms with a pronounced "shoulder", while samples degraded in the form of a film give a thermogram with a single peak. Furthermore, the freeze-drying procedure is time-consuming. It was therefore decided to study mixed and unmixed samples as films prepared by evaporation of a solution of the polymers in a common solvent, such as cyclohexanone or tetrahydrofuran. The technique

adopted by Mizutani was rejected, as being less likely to guarantee reproducible mixing.

(b) Comparison of Mixed and Unmixed Systems.

In any study of the degradation of mixed polymer systems, a method must be found of comparing mixed and unmixed systems under similar conditions.

An obvious approach to this problem would be to obtain TVA thermograms for known weights of the component polymers, and by addition, obtain the TVA thermogram expected of the mixture. This composite thermogram could then be compared with the thermogram actually obtained when the mixture is degraded. Any differences between the "theoretical and "experimental" thermograms could then be taken as an indication of interaction between the polymer pair.

However, the non-linearity of Pirani response, and the different response which the gauge head has towards different substances, means that the addition of two TVA traces in the manner described above is virtually impossible .

Some method must therefore be devised of heating known weights of the polymers simultaneously, but in an unmixed condition, and comparing the resulting thermogram with that obtained by the degradation of a blend consisting of the same weights of the two polymers.

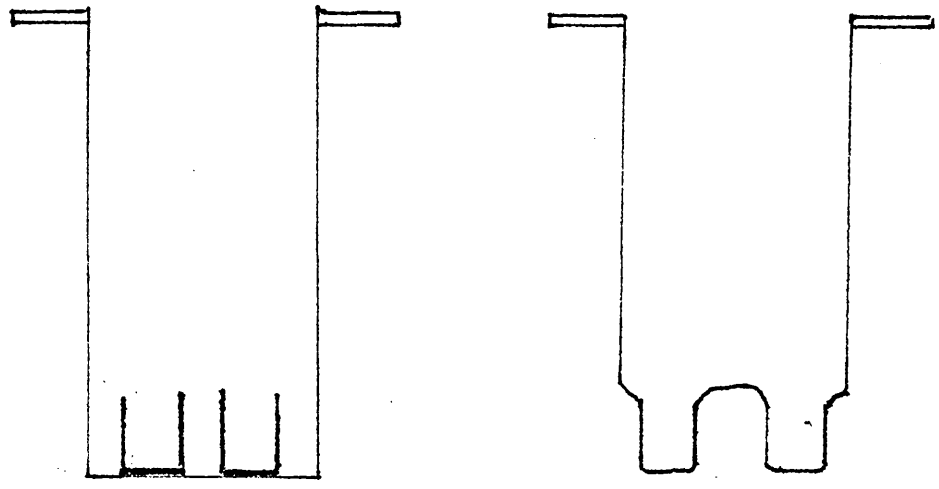
EXPERIMENTAL DETAILS.

Method of Comparing Mixed and Unmixed Systems.

Two techniques were used to compare mixed and unmixed systems, both following the general principle outlined above.

In most of the experiments described below, known weights of each polymer were placed in separate small flat bottomed Pyrex glass crucibles of sufficient size that two could be accommodated side by side in the large degradation tube (figure 7,1,a), and a TVA thermogram obtained in the usual way. The experiment was then repeated, with equal weights of the polymer blend in each crucible such that the total weight of each polymer was the same as in the previous experiment. Thus a comparison could be made of the thermogram obtained by degrading the two polymers simultaneously, but unmixed, with the thermogram for the polymer blend, under the same conditions.

As would be expected, the glass-glass surface caused an increase in the temperature differential between the oven thermocouple and the sample area. Comparison of the thermograms obtained by degrading standard samples in such a crucible, with those obtained when the sample was placed directly on the tube base, showed that the additional thermal lag was reproducible, and amounted to 10°C, at a heating rate of 5°/min, which was not



(a) (b)

FIGURE(7,1), Sample crucibles for the study of polymer blends by TVA.

considered to be excessive. Somewhat surprisingly, the temperature differential was not reduced when the crucibles were placed on a layer of copper powder, suggesting that the lag was due to the additional glass surface, rather than bad contact between the base of the tube and the crucible.

An alternative approach, also used in this study, was to employ a redesigned degradation tube, in which crucibles of the type described above were incorporated directly into the base of the tube, in place of the usual flat base, as shown in figure (7,1,b). This approach avoids the additional temperature lag described above. As with the crucibles, care was taken to ensure that the glass surfaces in both limbs of the tube were of similar thickness, so that samples in each limb (or crucible) had, as far as possible, the same thermal environment. Calibration experiments, of the type described in Chapter 2 were carried out to ensure that the thermal lag was the same for each limb.

Method of Preparing Samples for Degradation.

The usual method of sample preparation was as follows: Solutions of the two polymers under study, of known concentration (usually 10 mg/ml) were made up in cyclohexanone or tetrahydrofuran. (Both solvents were of commercial grade, twice distilled before use). A mixed solution of the two polymers was

then obtained by combining equal volumes of the two solutions, and shaking thoroughly. At the concentrations used in this study, (normally the total concentration of polymer was no greater than 20 mg/ml) phase separation was not observed in the mixed solutions, even when they were left to stand for a period of a week.

For the study of the unmixed polymers, equal volumes of the two solutions were placed in separate crucibles, and the solvent removed, either by continuous pumping in a vacuum oven, at room temperature (cyclohexanone) or under a continuous stream of oxygen-free nitrogen (tetrahydrofuran), again at ambient temperatures. The crucibles were then lowered onto the base of the degradation tube, and a TVA thermogram obtained in the usual way.

For the mixed polymer system, the same crucibles were used, after the residue from the previous experiment had been removed. The mixed polymer solution was shaken thoroughly, equal volumes were placed in the separate crucibles, and polymer films obtained as before.

The resulting mixed films were opaque, confirming the incompatibility of the polymer pair. However the films were continuous and even, as were the residues from degradation. Furthermore, the reproducibility of the TVA thermograms obtained confirmed that reproducible sample preparation was achieved by this procedure.

Polymers Used.

Details of the polymers used in this investigation are given in Appendix 1.

TVA EXPERIMENTS.

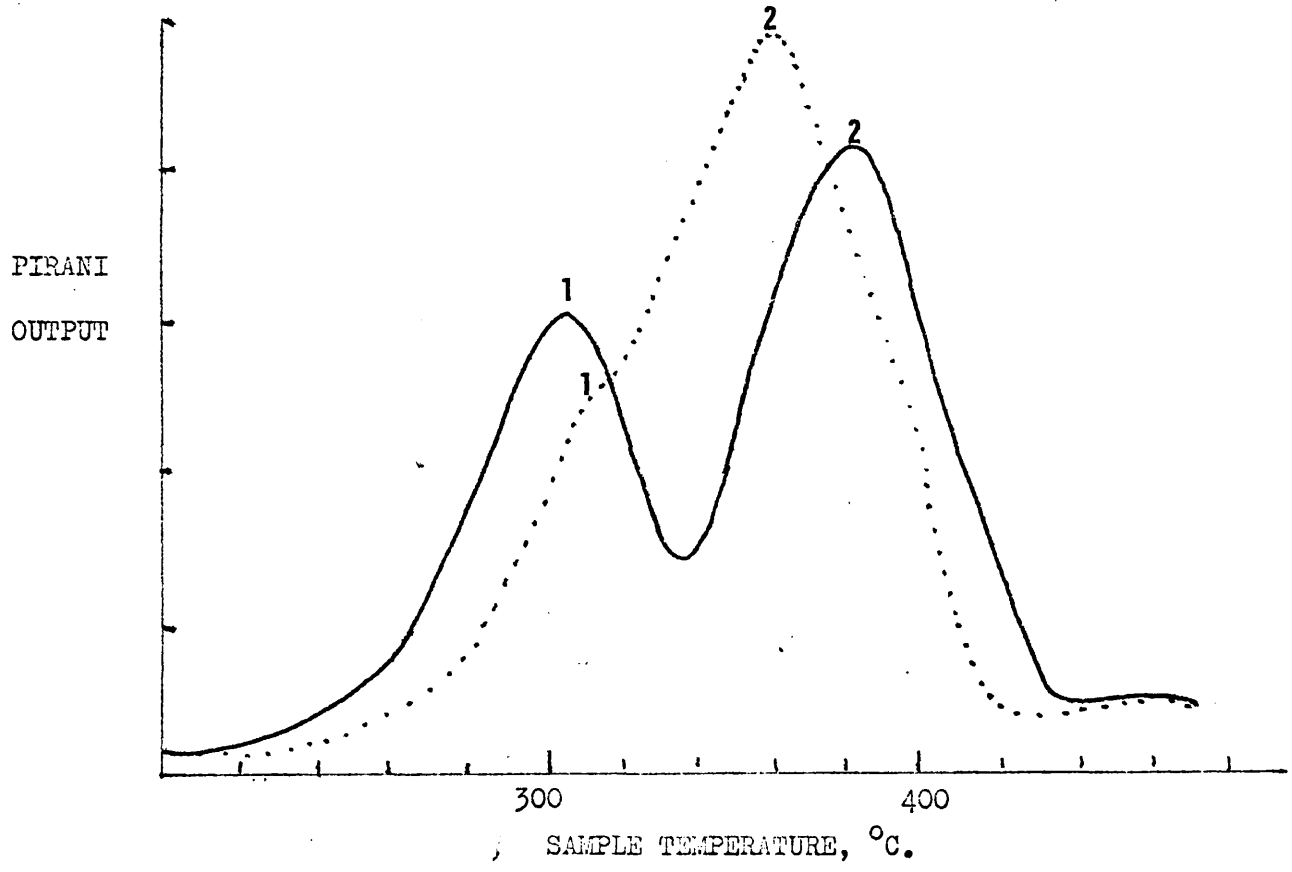
Initial Experiments.

Using the method of sample preparation described above, 5 mg samples of PMMA anionic, and PVC 113 were degraded (a) simultaneously, but unmixed, and (b) as a blend, using the same ~~conventional~~ TVA system. The thermograms so obtained are shown in figure (7,2).

Denoting the peaks in the thermograms as shown in figure (7,2) we can summarise the changes which occur on blending the two polymers as follows:-

(a) In the TVA thermogram for the polymer blend, peak 1 increases in height at Tmax., and moves to slightly lower temperatures (316°C in unmixed polymers, 307°C in mixed polymers) i.e. there is a substantial increase in the production of volatile material from the mixture in this temperature range.

(b) Peak 2 is reduced in height in the blended polymers, and the rate maximum shifts to higher temperatures i.e. in this temperature range, the mixed system yields a smaller amount of volatile material than the unmixed polymers.



FIGURE(7,2), TVA thermograms (at 5°/min.) for PMMA anionic and PVC 113. 5mg of each polymer were used.

---------- Simultaneous degradation of unmixed polymers as separate films.

———————— Degradation of mixed polymer films, under the same conditions.

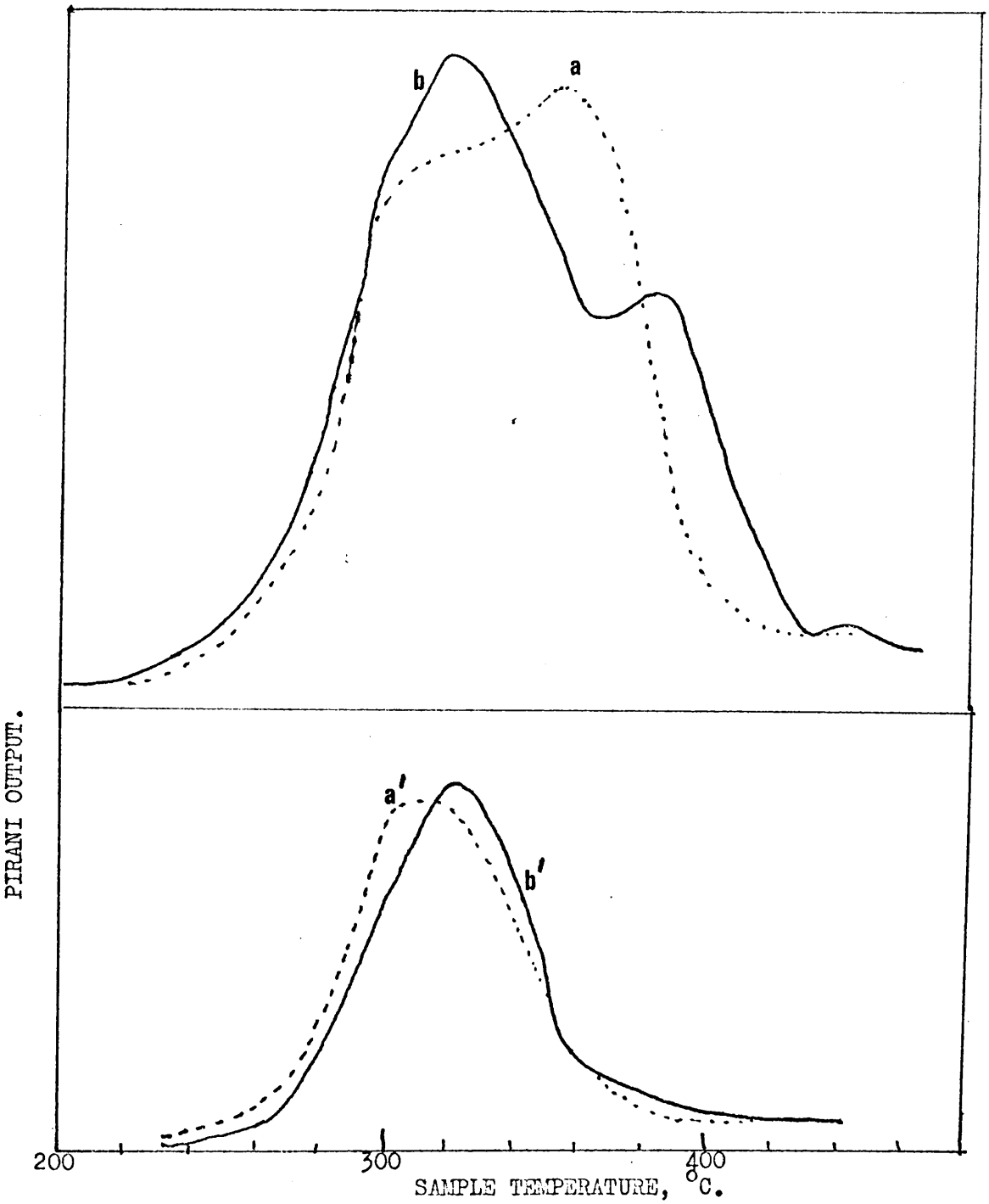
Polymer solutions were made up again, and mixed and unmixed samples degraded as before. The resulting thermograms showed that the behaviour described above was typical and reproducible for the polymer pair.

The use of Different Cold Trap Temperatures.

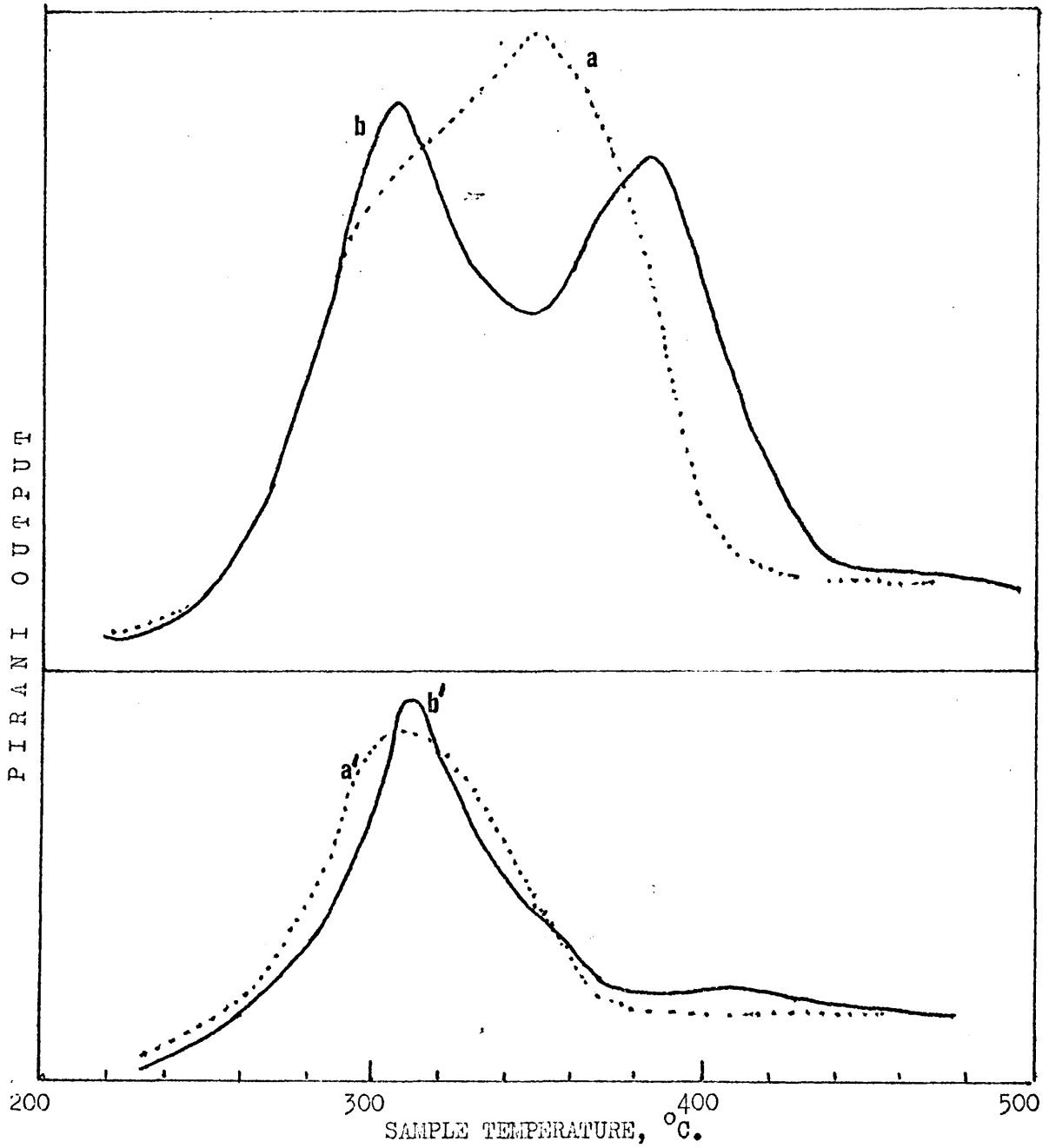
(a) Cold trap at - 100°C.

Further information on the nature of the interaction between the two polymers was given by recording the output from a Pirani gauge placed beyond a cold trap at - 100°C (socket J, figure (2,1 - page 40). Previous experiments had shown that although methyl methacrylate was effectively condensed by such a cold trap, hydrogen chloride was not (see Table 2,3 - page 65).

Thermograms obtained in this way are shown in figures 7, 3 and 7,4. The traces a and b are the outputs from a Pirani gauge placed between the sample and the cold trap, for unmixed and mixed systems respectively. Traces a' and b' were obtained from the Pirani gauge placed after the trap. It should be noted that since the gauges are not in equivalent positions, the traces for total volatiles and non-condensable material are not directly comparable. However, the point which clearly emerges from these thermograms is that the increased volatilisation in the early stages of degradation of mixed samples is due to the production



FIGURE(7,3), TVA thermograms (at 5°/min.) for PMMA FRI and PVC 113. 10mg of each polymer were used. Trace a: simultaneous degradation of unmixed polymers as separate films. Trace b: degradation of films with mixed polymers. Traces a' and b': as for a and b, except that a -100°C trap was placed before the attachment point of the Pirani gauge.



FIGURE(7,4), TVA thermograms for PMMA anionic and PVC 101. Other details as given in caption for Figure(7,3).

of condensable, rather than non-condensable material. Indeed the production of non-condensable material is slightly delayed, rather than increased, in mixed samples.

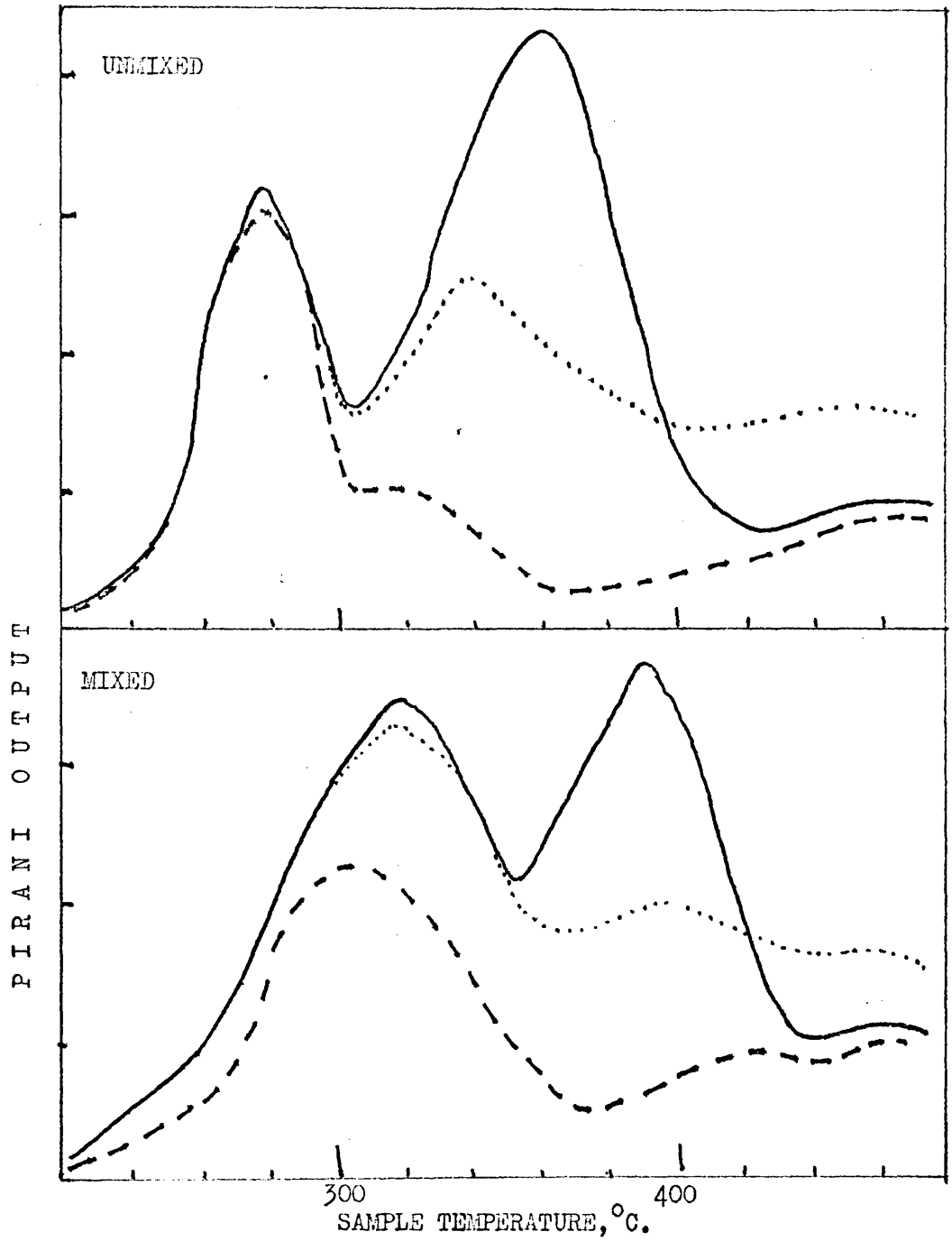
(b) DC - TVA Thermograms.

Thermograms for mixed, and unmixed samples were obtained using the Differential Condensation Apparatus, with cold traps at 0°, -45°, -75° and $-100^{\circ}C$. A typical thermogram is shown in figure (7,5). It can now be seen that the first peak in unmixed samples is due entirely to material which is not condensed at $-100^{\circ}C$, and corresponds to the major degradation peak of PVC. The second peak in unmixed samples is due to the production of methyl methacrylate, which shows as a steady "vapour pressure" on the -75° trace.

In mixed samples, the first peak is increased in height, and is clearly associated with an increase in the production of non-condensable material. In mixed samples, the breakdown at higher temperatures again involves the production of methyl methacrylate, although less volatile material is evolved. The production of HCl from mixed films is again delayed, and there is a tendency for a greater amount of non-condensable material to be evolved in the later stages of degradation of the polymer blend.

Effect of varying type of polymer.

Studies were made of the effect of the type of polymer



FIGURE(7,5), DC-TVA thermograms for mixed and unmixed samples of PMMA FRI and PVC 113,20 mg. of each polymer. Heating rate was 10°/min.
For key to the representation of Pirani traces, see Figure(6,1)

used on the nature of the interaction in mixed systems. In each case tested, an interaction was observed, of the same type as discussed above. The list below shows the variety of PVC and PMMA samples which gave interactions.

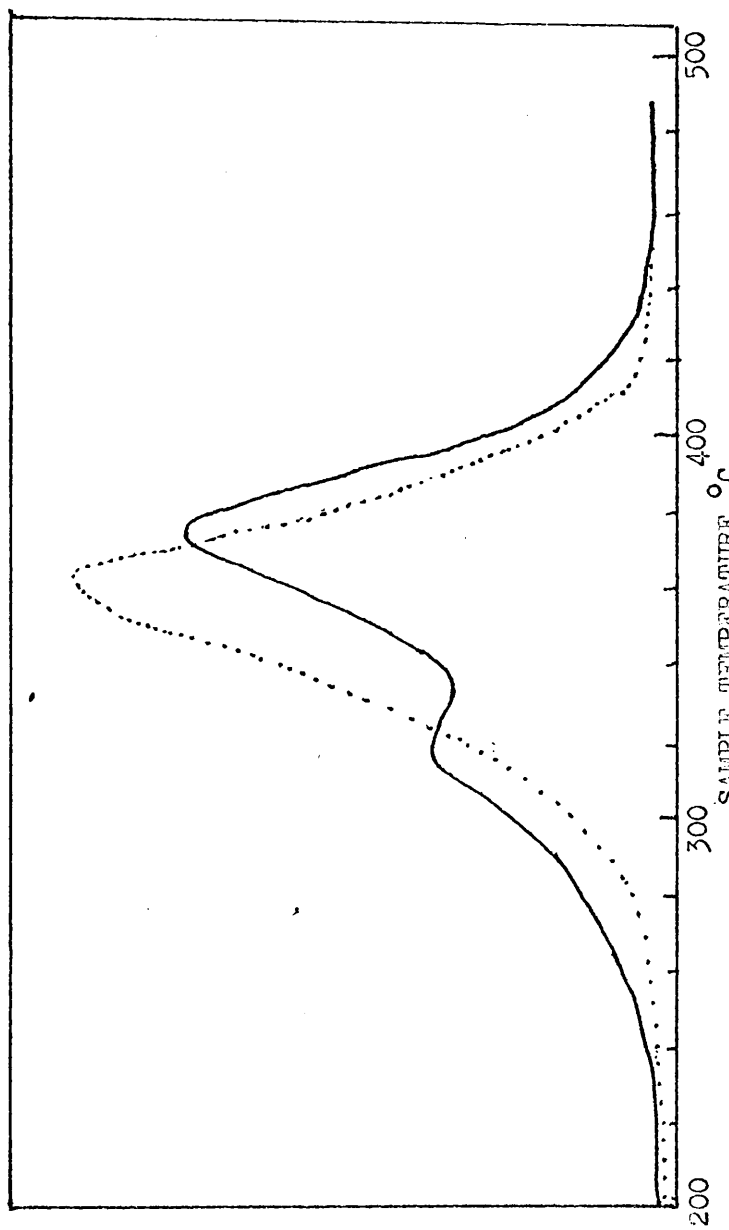
PVC 113; PVC 101; PVC 111; PVC 121; PVC 176A;

PMMA anionic; PMMA FRI; PMMA DF;

Any of the PVC samples listed above, with any of the PMMA samples mentioned, were found to give a similar interaction in mixed films. It would therefore appear that this behaviour is characteristic of the polymer pair. It was not attempted, however, to relate the molecular weight of either polymer to the magnitude of the observed interaction (this would in any case be difficult, owing to the non-linearity of the Pirani gauge output).

Effect of Varying the Relative Proportions of the Two Polymers.

In the experiments discussed so far, equal weights of PVC and PMMA were used to obtain thermograms for mixed and unmixed systems. Thermograms for 1:10 PVC : PMMA mixtures (by weight) are shown in figure (7,6), compared with unmixed samples. It is clear that even this small quantity of PVC is capable of reducing considerably the thermal stability of PMMA. Again the later stages of breakdown involve the production of less volatile material, and the displacement of the degradation peak to higher temperatures.



FIGURE(7,6), Thermograms for 1mg. of PVC 113 with 10mg PMMA FRI, in mixed and unmixed conditions (5°/min.)

- - - - - - simultaneous degradation as separate films of the unmixed polymers.

——— degradation of the polymers as a mixed film.

The effect of varying the ratio of the polymers in the mixture was not systematically investigated. However, it was noted that in the decomposition of a 3:1 mixture of PVC : PMMA, the second degradation peak was displaced to slightly higher temperatures than in 1:1 mixtures.

Effect of Heating Rate.

The usual heating rate employed in these investigations was 5°/min. It should be noted, however, that the DCTVA thermograms shown in figure (7,5) were obtained at a heating rate of 10°/min. Experiments conducted at 2°/min confirmed that qualitatively, the nature of the interaction between the two polymers was independent of heating rate.

The Effect of Solvent System Used.

In most of the experiments reported in this Chapter the solvent used to prepare the polymer blends was cyclohexanone. It was found that the films prepared using this solvent had a more even appearance than those prepared by evaporation from tetrahydrofuran solution.

However, considerable precautions had to be taken to ensure that the cyclohexanone used was completely free from impurities. When TVA thermograms were run of PMMA samples, cast as films from unpurified cyclohexanone, it was found that a "cold-ring fraction"

identified by IR spectros copy as low molecular weight polymer, was obtained. Since films cast from benzene gave no such product fraction on degradation, it must be concluded that impurities in the cyclohexanone were capable of initiating chain scission in the polymer. In all probability the species responsible were peroxides formed by autoxidation of the cyclohexanone during storage.

It was found that freshly distilled cyclohexanone produced no cold-ring fraction in PMMA. All efforts were therefore made to ensure that polymer solutions were prepared from freshly distilled cyclohexanone, and TVA thermograms were obtained as soon as possible after the solutions were made up.

The interaction between the two polymers was found to be independent of the solvent system used to prepare the films. For example, the DCTVA thermogram in figure (7,5) was obtained using films cast from tetrahydrofuran.

Study of blends of the powdered polymers.

(a) Examination by TVA.

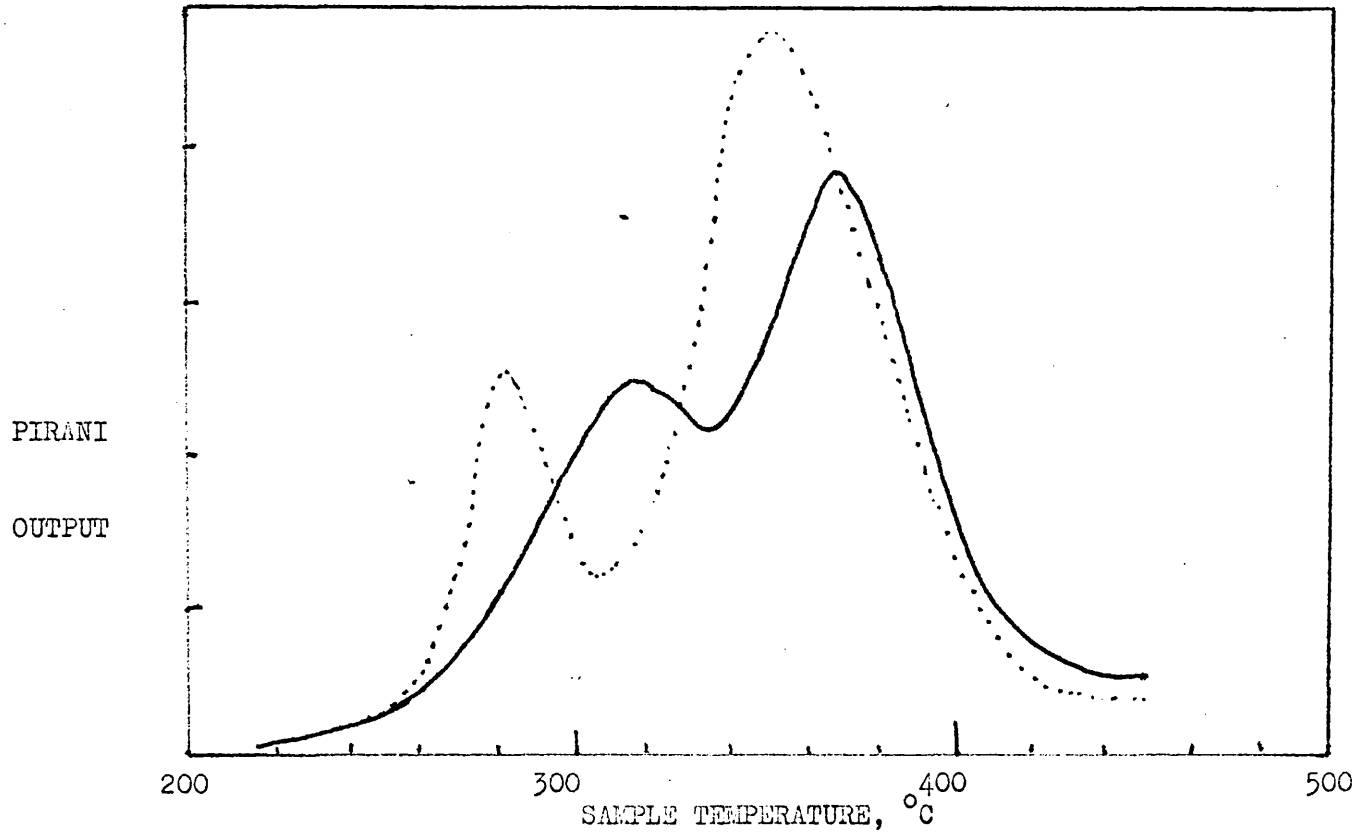
For the reasons discussed earlier, mixed and unmixed samples were usually degraded as films. Limited investigations were carried out to see if any interactions occurred in blends of the powdered polymers.

Samples of PMMA (anionic and F.R.I.), and PVC 113 were ground

to fine powders capable of passing through a 0.0049 in. mesh. A blend of the two polymers was obtained by placing equal weights of the two powders in the same container, and stirring for one hour. TVA thermograms were then obtained for the degradation of equal weights of the two polymers in mixed and unmixed conditions. These are shown in figure (7,7). Clearly there is some form of interaction in mixed samples, although it does not take exactly the same form as in film samples. The complicating factor in this case is the effect of sample form on the TVA thermogram of PVC. However, it would appear that the interaction between the two polymers is qualitatively similar to that observed in mixed films.

(b) TG Studies.

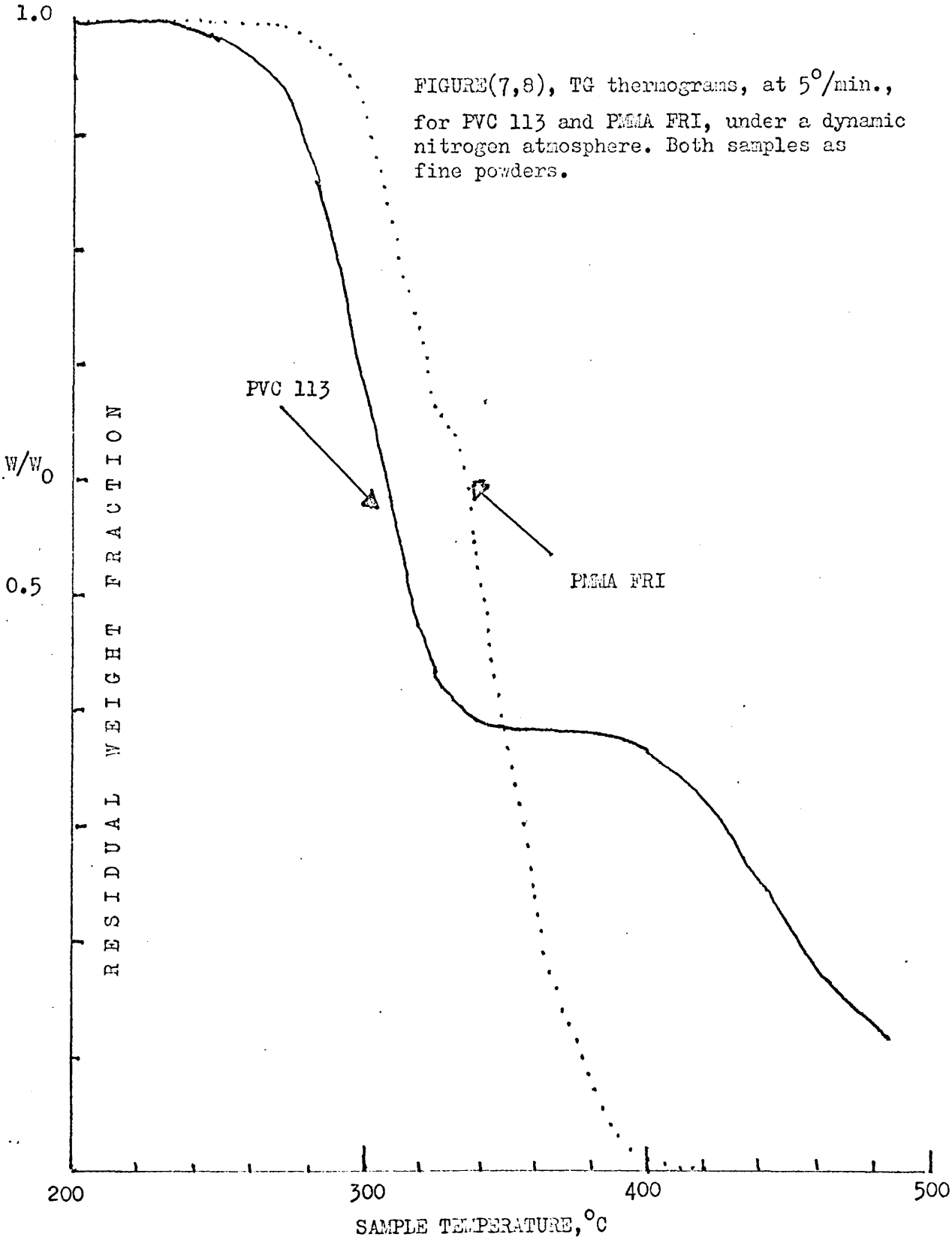
TG thermograms were obtained, using the Du Pont 950 Thermogravimetric Analyser for PMMA anionic and PVC 113 samples, as powders, and are shown in figure (7,8). From these thermograms, the thermogram which would be expected for a 50-50 mixture of the two polymers was constructed. This is compared with the actual experimental thermogram for the mixed powders in figure (7,9). Again, the weight loss of the polymer blend is different from that expected in the absence of interaction between the polymer pair. The weight loss of the mixed sample, in the temperature range 320 to 340°C, is greater than is predicted by the composite



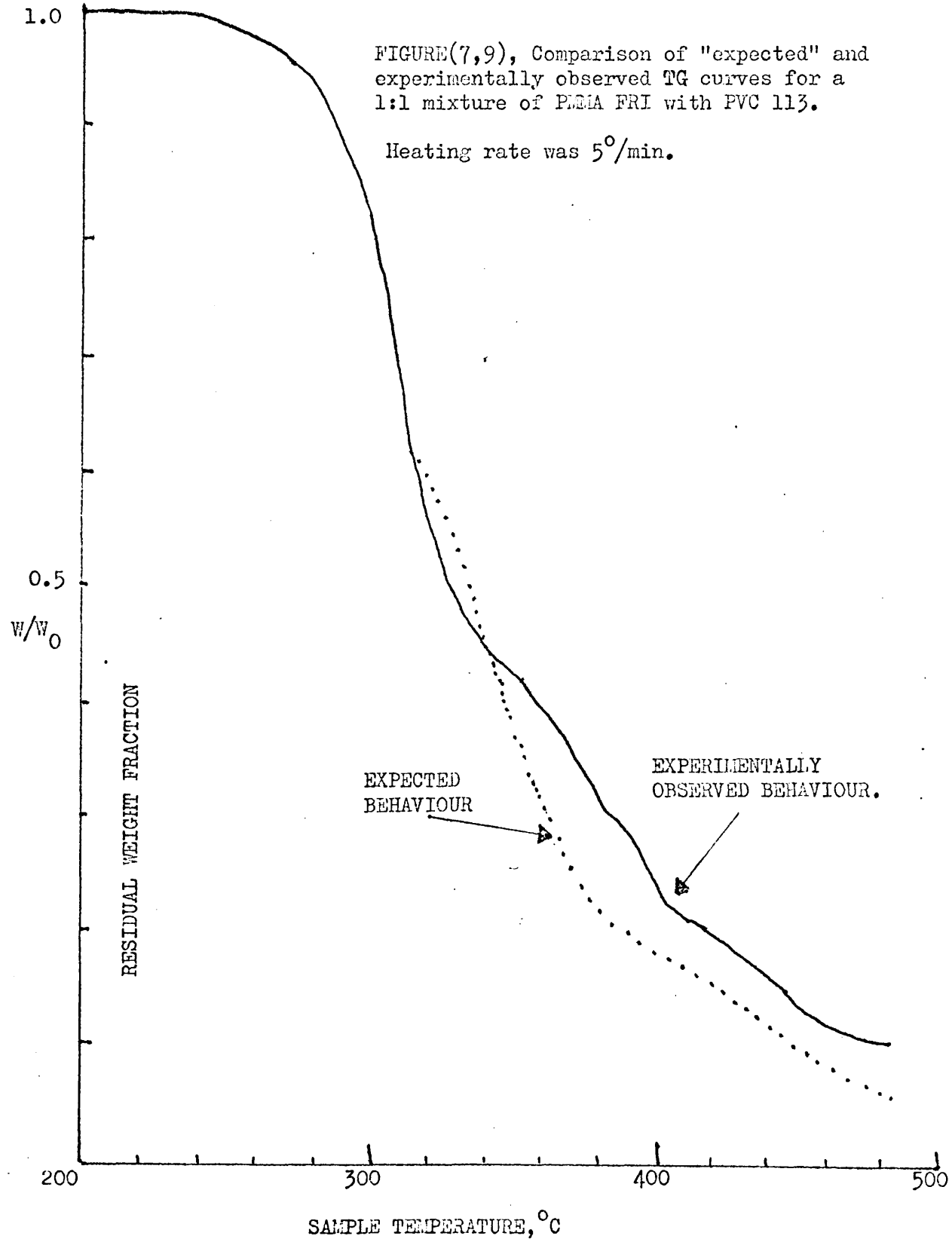
FIGURE(7,7), Degradation of mixed and unmixed samples of PVC 113 and PMMA anionic. 5mg of each polymer were used. Both polymers were in the form of a powder, capable of passing through a 0.0049in. mesh. A heating rate of 5°/min. was used.

- - - - - - - - - simultaneous degradation of the unmixed powders in separate crucibles

——————— degradation of a mixture of the two powders under the same conditions.



FIGURE(7,8), TG thermograms, at 5°/min., for PVC 113 and PMMA FRI, under a dynamic nitrogen atmosphere. Both samples as fine powders.



FIGURE(7,9), Comparison of "expected" and experimentally observed TG curves for a 1:1 mixture of PMMA FRI with PVC 113.

Heating rate was 5°/min.

thermogram. Above 350°C, however, the weight loss from the polymer blend is less than would be predicted.

Unfortunately, the Du Pont instrument, in its present form is not suitable for the study of samples prepared in the form of films, owing to the size and shape of the sample container. It was therefore impossible to compare the behaviour of film and solid samples by TG.

Owing to the difficulties in accurately weighing small samples, the unsatisfactory method of preparing mixed samples by combining the powdered polymers, and the effect of sample form on the TVA thermogram for PVC, no further studies of mixed powdered samples were undertaken.

Effect of the Residue from PVC Degradation on the Decomposition of PMMA.

Since the production of hydrogen chloride (as detected by the - 100°C Pirani) in mixed and unmixed films is not greatly altered, the interaction in mixed systems can be regarded as being one involving the destabilisation of PMMA by PVC. It is of interest to observe whether the interaction is associated only with the dehydrochlorination of PVC, or whether the residue so produced can destabilise PMMA. A powdered sample of PVC 113 was heated through the first degradation peak, and allowed to cool.

10 mg. samples of both PMMA and the PVC residue were then degraded in mixed, and unmixed conditions. Since the residue from PVC degradation was insoluble, the mixed sample was prepared by evaporating to dryness a slurry made of the residue in PMMA solution.

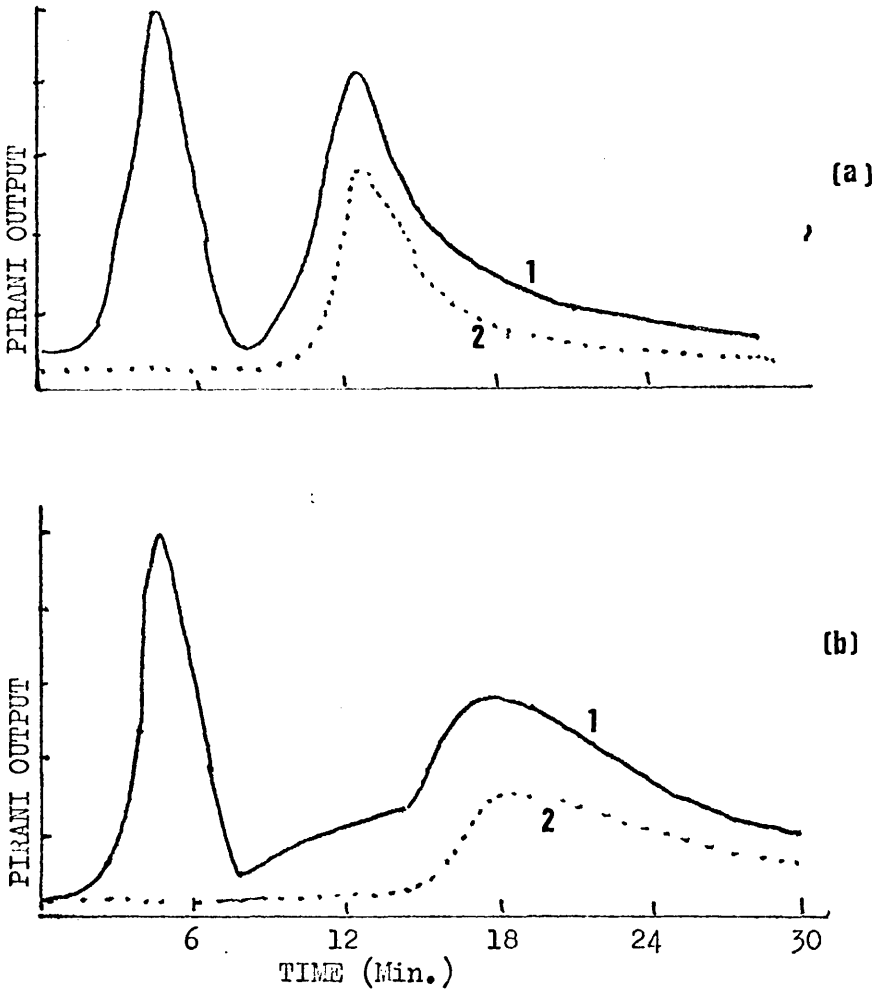
No difference was observed in the mixed and unmixed thermograms, suggesting that the PVC - PMMA interaction is associated with HCl production, and not caused by the carbonaceous residue.

The Use of TVA Isothermally.

Most of the thermograms obtained in this study were obtained under temperature programmed conditions. Some thermograms were obtained under isothermal conditions, however, and these are shown in figures (7,10) and (7,11).

In figure (7,10 (a)), the Pirani outputs from gauge heads placed before and after a cold trap at - 100°C are recorded, for the degradation of unmixed samples of PMMA FRI and PVC 113 (10 mg. of each), and in figure (7,10 (b)), are shown the Pirani outputs under the same conditions for the mixed polymers. The oven temperature was in each case, 320°C.

Comparison of the two thermograms clearly shows that the rate of production of non-condensable material from the mixed

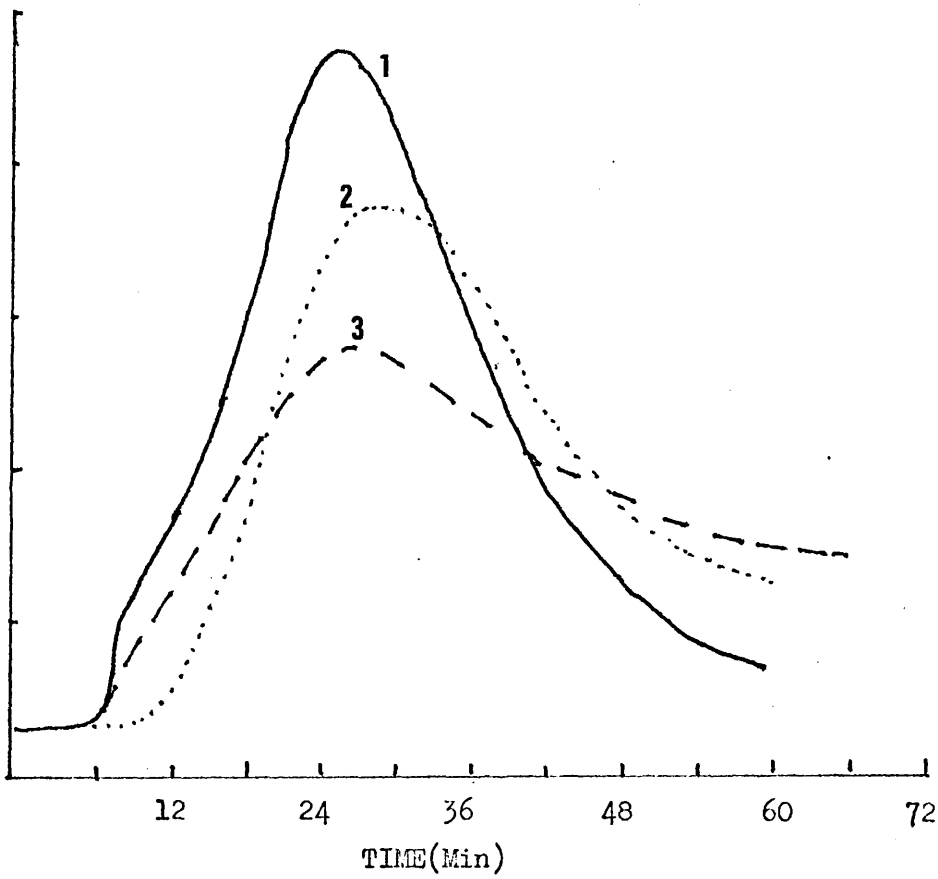


FIGURE(7,10), Isothermal degradations (at 320°C) of each of PMMA anionic and PVC 113 (a)as separate, unmixed films, (b) as mixed films.

1 : Output from Pirani placed between cold trap and sample.

2 ; Output from Pirani placed after a cold trap at -100°C

Note Since the Piranis are not in equivalent positions,(H and J, respectively, Figure(2,1)), the response of 1 will be greater to the same flow rate, than the response of 2.



FIGURE(7,11), Effect of small amounts of PMMA FRI on the isothermal dehydrochlorination of PVC 113, at 270°C.

1 : PVC 113, 100mg
2 : PVC 113, 100mg + 10mg PMMA
3 : PVC 113, 100mg + 30mg PMMA.

polymers is considerably reduced, and the onset of production of non-condensable material is noticeably delayed.

Furthermore, it should also be noted that after elimination of solvent from mixed films, there is a short period of time during which condensable material is evolved from the film, before the onset of production of non-condensables. By contrast, the Pirani traces for total volatiles and non-condensables in unmixed samples depart from the base line simultaneously.

Clearly the delay in the production of non-condensable material from mixed films is more marked in isothermal experiments. In figure (7,11) the Pirani output from a gauge head placed beyond a cold trap at - 100°C is recorded for the degradation at 270°C of 100 mg. of PVC 113, together with the traces obtained when the same weight of polymer was heated in the presence of 10, and 30 mg. of PMMA FRI. It is obvious from these thermograms that even the presence of such small quantities of PMMA is capable of delaying the production of HCl from mixed samples.

Summary of TVA Evidence.

On the basis of the TVA evidence presented so far, it is possible to make the following observations on the nature of the interaction between the PVC - PMMA pair:-

(1) In the early stages of decomposition, mixed films of PVC

and PMMA liberate an increased amount of volatile material, condensable at - 100°C, than is evolved from the unmixed polymers.

(2) However, in the later stages of breakdown of the mixed polymers, less volatile material is evolved, and the rate maximum is displaced to higher temperatures.

(3) There is a tendency for the production of HCl from mixed films to be delayed. Even very small quantities of PMMA are capable of delaying the production of HCl from PVC. However, the total amount of HCl evolved from mixed films appears to be the same as that evolved from the unmixed polymers.

(4) Even small quantities of PVC are capable of initiating the decomposition of PMMA.

(5) The interaction is characteristic for all samples of PMMA and PVC tested, and is independent of the solvent system used to prepare the films.

(6) The interaction between the polymer pair takes the same form, independent of the heating rate employed.

(7) The polymers are also capable of interacting when in the form of powders.

(8) The interaction is associated with the evolution of HCl from PVC, since the residue from dehydrochlorination is not capable of initiating the decomposition of PMMA.

PRODUCT ANALYSIS - VOLATILE PRODUCTS.

Infra-Red Gas Cell Analysis.

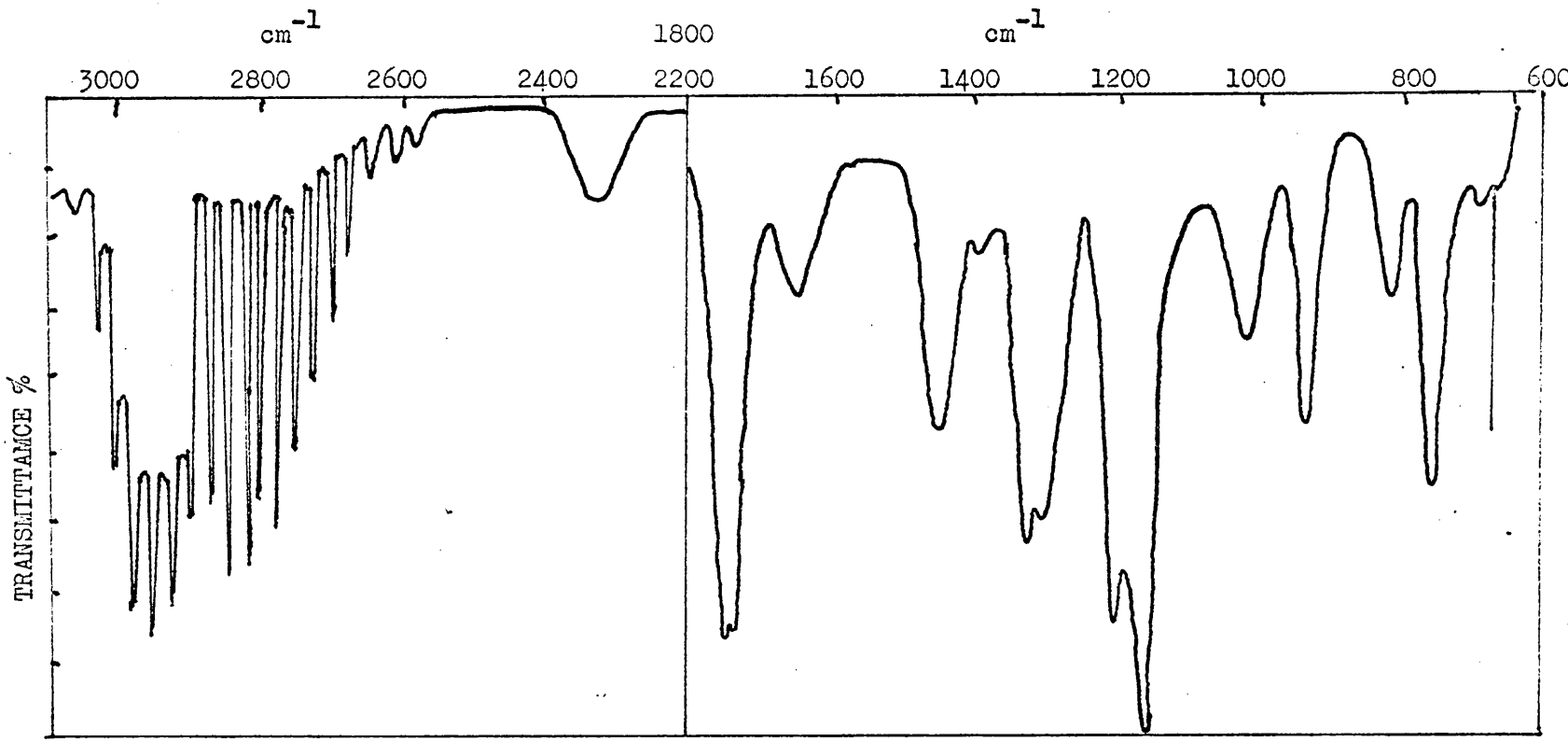
(a) Products from Temperature Programmed Experiment.

100 mg. of PMMA anionic and 100 mg. PVC 113 were heated, as a mixed film, in the TVA apparatus, at 5°/min to 500°C. (The residual solvent in the film had previously been removed by heating the film to 200°C). The products from this degradation were trapped out at liquid nitrogen temperature, distilled into an infra-red gas cell, and the spectrum run. This is shown in figure (7,12). The characteristic band spectrum of HCl is evident, in the region 3050-2600 cm^{-1} strong peaks at 1750, 1180 and 1210 cm^{-1} can be attributed to methyl methacrylate, and peaks at 2320 and 670 cm^{-1} to carbon dioxide.

(b) Products from Isothermal Experiment.

The infra-red spectrum of products from the pyrolysis of a similar mixed film at 210°C for four hours was found to be qualitatively similar to that described above, although no carbon dioxide was present, and the peaks were of lower intensity.

With the exception of carbon dioxide, the products identified by IR analysis are the same as the products evolved by the unmixed polymers. Since the increased volatilisation in mixed films is due to the production of material which is condensable at -100°C, it would appear that the substance evolved at this stage is methyl methacrylate.



FIGURE(7,12), Infra-red spectrum (gas cell) of the products of degradation to 500°C, of a PMMA anionic - PVC 113 mixed film.

Mass Spectrometric Analysis.

The products of degradation of a mixed film of PVC 113 and PMMA FRI were subjected to mass spectrometric analysis. Again, residual solvent was removed from the film by preheating to 200°C. The products resulting from the degradation of the mixed film at 5°/min, to a temperature of 500°C were then collected in two fractions.

(a) Products condensed by a trap at -100°C.

(b) Products non-condensable at -100°C but condensed at liquid nitrogen temperature.

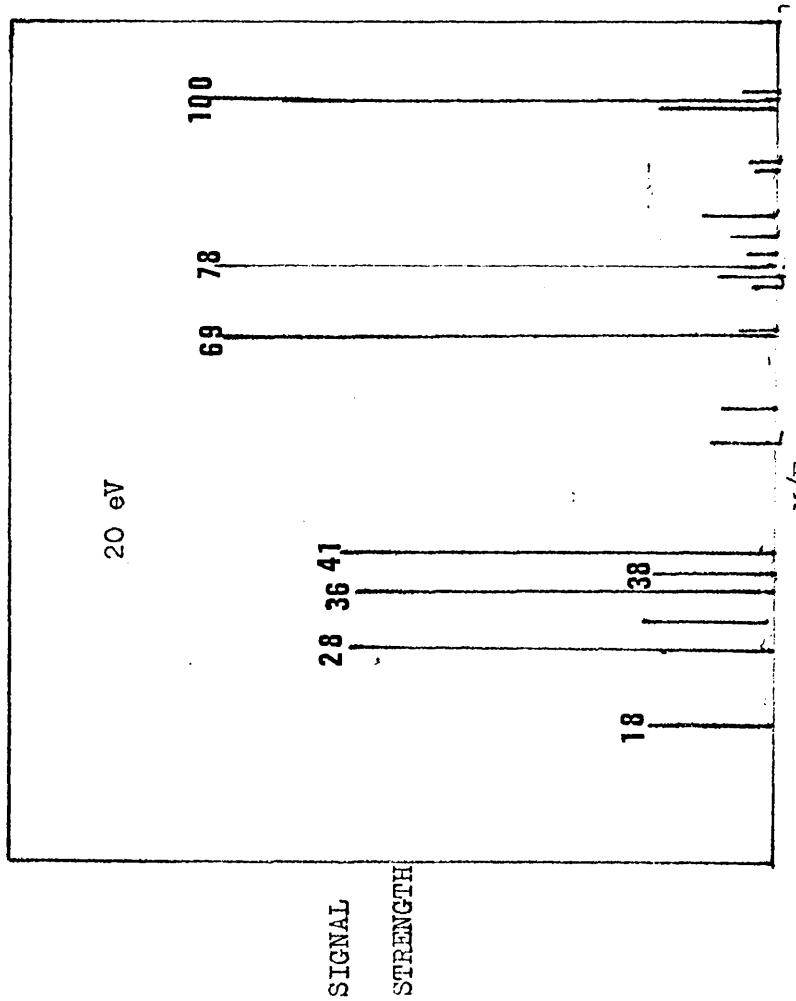
Each product fraction was collected by distillation into a suitable gas sampling bulb, and the mass spectra were obtained for the samples, as gases, on an AEI MS12 mass spectrometer operating at 20 eV. The spectra for fractions (a) and (b) are reproduced schematically in figures (7,13) and (7,14) respectively.

Interpretation of Spectra - Fraction (a).

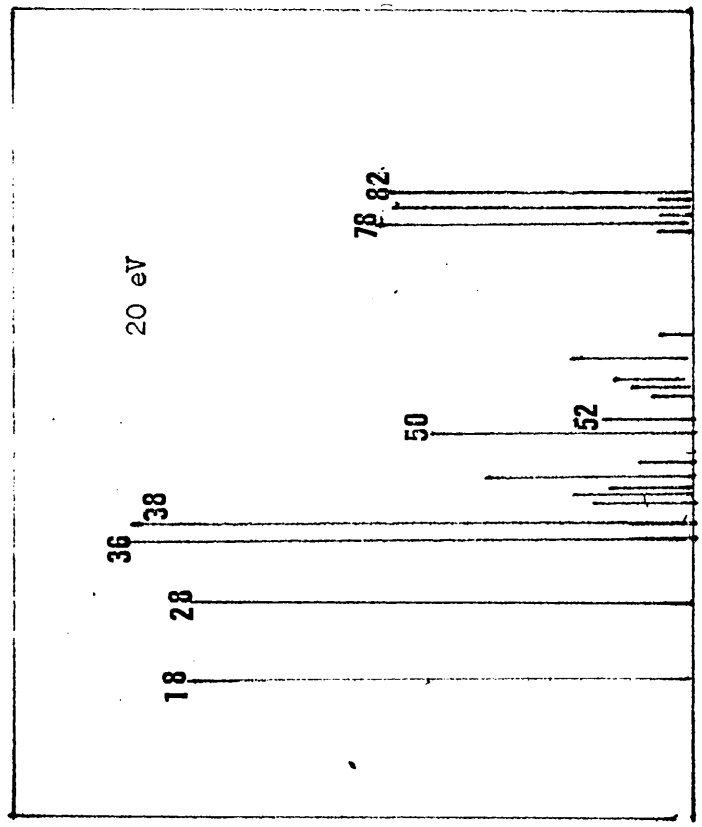
Signals at m/e values 100 ($CH_2 = \underset{CH_3}{\overset{|}{C}} - \underset{O}{\overset{\|}{C}} - O - CH_3$);

69 ($\underset{O}{\overset{\|}{C}} - \underset{CH_3}{\overset{|}{C}} = CH_2$); and 41 ($\underset{CH_3}{\overset{|}{C}} = CH_2$);

can be attributed to methyl methacrylate. Peaks at m/e 36 and 38 are due to $H^{35}Cl$ and $H^{37}Cl$ respectively. The peak at 78 is



FIGURE(7,13), Mass spectrum of products of degradation of a PMMA-PVC mixed film
(Fraction condensed at -100°C.)



FIGURE(7,14), Mass spectrum of products of degradation of a PMMA - PVC mixed film.

(Fraction not condensed at -100°C, but condensed by a trap at liquid nitrogen temperature.)

presumably due to benzene, from the breakdown of aromatic structures in the carbonaceous residue from PVC degradation.

Fraction (b)

Methyl methacrylate is absent, being fully condensed in the -100°C trap. Strong signals present at m/e 36 and 38 are again attributable to HCl, and the signals at 78 are due to the presence of benzene. Peaks and 50 and 52, of which the former is of greater intensity are probably due to $CH_3{}^{35}Cl$ and $CH_3{}^{37}Cl$ respectively. The small peaks at 80 and 82 are possibly due to cyclohexadrene and cyclohexene respectively, formed in the same process as leads to the evolution of benzene. The small peak at 44 m/e may be due to carbon dioxide, as was detected by IR spectroscopy.

Significance of mass spectrometric data.

Unfortunately it was not possible to determine the relative proportions of the various products using mass spectrometry, since calibration experiments could not be carried out. The spectra can therefore only be used as a qualitative guide to the various species present.

Clearly, however, fraction (a) consists predominantly of methyl methacrylate, although a small amount of benzene and hydrogen chloride has been retained by the -100° trap. Since the formation of benzene is associated with the high temperature

breakdown of the residue produced by dehydrochlorination of PVC, again it must be concluded that the increased volatilisation in the early stages of breakdown of mixed films is due to the production of methyl methacrylate.

The presence of methyl chloride in fraction (b) is in agreement with the studies of Zutty and Welch [85], who observed that small amounts of this compound were formed from the pyrolysis of PVC-PMMA blends. However, the studies of the copolymers of vinyl chloride and methyl methacrylate, discussed in the previous chapter showed that methyl chloride was not condensed by a trap at -100°C (otherwise it would have appeared in fraction (a). Hence the increased volatilisation in mixed films cannot be attributed to the formation of this compound.

Analysis of Products by Gas-Liquid Chromatography.

The products of degradation (a) from PMMA anionic, and (b) from a PMMA-PVC 113 blend containing equal weights of the two polymers, were studied by GLC. In each case, the sample was heated, at 5°/min to a sample temperature of 330°C (i.e. just after the first peak in mixed films). The products were trapped at liquid nitrogen temperature, and stored in a narrow bore receiver.

GLC chromatograms were obtained on using a 1% SE30 column, and a flame ionisation detector, with nitrogen as carrier gas. The

chromatographic column was programmed at 10°/min, the programme being started immediately after sample injection. Only the products which were liquid at room temperature were investigated.

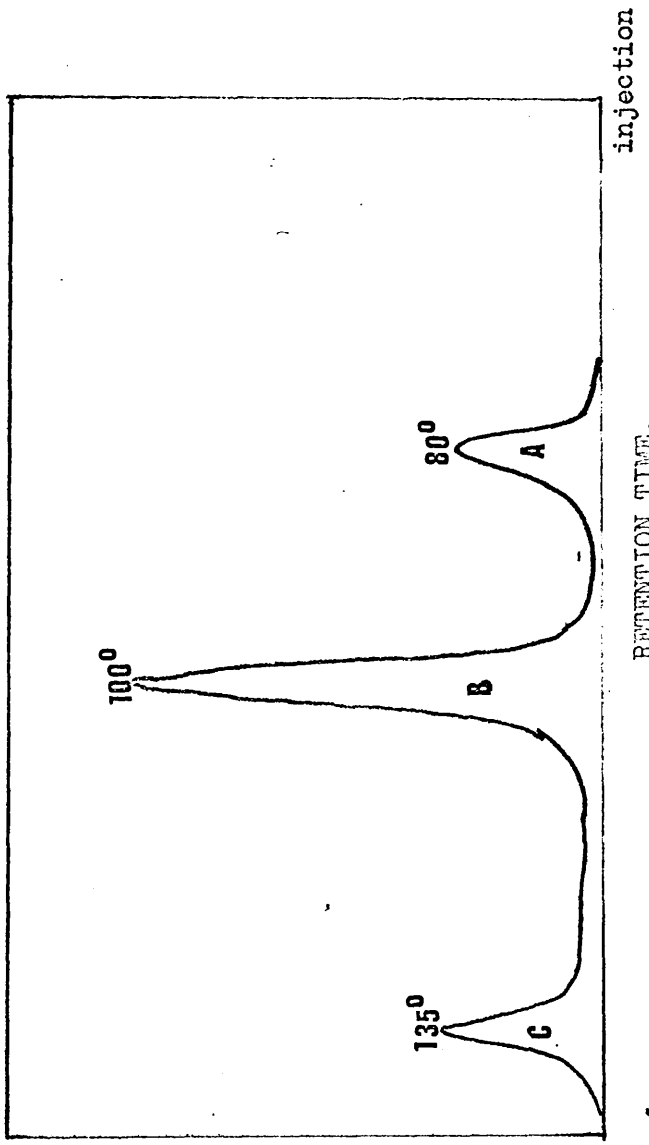
A typical chromatogram, for the products from a mixed sample, is shown in figure (7,15). Peak A, which appeared only in the products from mixed samples, had the same retention time as HCl. Peak B, which appeared in the chromatogram for PMMA products, had the same retention time as methyl methacrylate, while peak C had the same retention time as cyclohexanone.

Since MMA and HCl are the only products evolved from the polymer blend during the early stages of volatilisation, it must again be concluded that the increased volatilisation in the blend is due to monomer production, initiated in some way by the degrading PVC.

STRUCTURAL CHANGES OCCURRING IN THE RESIDUE.

Molecular Weight Changes.

Three 100 mg. samples of PMMA anionic were heated at 5°/min to a sample temperature of 330°C, and rapidly cooled. The residue was then dissolved in "analar" toluene, and the concentration of the solution estimated (by evaporating a known weight of the toluene solution to dryness, and determining the weight of polymer present). The molecular weight of the degraded polymer was then measured,



FIGURE(7,15), GLC chromatogram of the products of degradation of a mixed film of PMMA and PVC.

using a "Mechrolab" High Speed Osmometer, Model 501, fitted with a Sylvania 300 grade cellophane membrane.

The same weight of PMMA was then heated under identical conditions as a mixed film with PVC 113. The residue, which was dark brown in colour, was removed from the degradation tube, and extracted with toluene, under continuous shaking, over a period of 48 hours. The solution was then filtered, and the concentration, and molecular weight, determined as before.

At no time were the toluene extracts heated, so that solvent induced molecular weight changes in the polymer were avoided.

PVC is almost completely insoluble in toluene and since the PVC sample used had previously been extracted with toluene, as detailed in Appendix 1, it could reasonably be assumed that the polymer removed from the polymer blend consisted almost completely of PMMA.

The results of this investigation, and those for a similar study of PMMA FRI - PVC 113 blends are shown in table (7,1 (a)) and (7,1 (b)) respectively. It is clear that in the presence of thermally degrading PVC, PMMA samples undergo a rapid fall in molecular weight, compared with the pure polymer.

Experiments were conducted in a similar manner, under isothermal conditions, at 190°C, the molecular weight of the toluene

T A B L E (7,1)

(a) The effect on the molecular weight ($\overline{M}_n$) of PMMA anionic of being heated (at 5°/min) to 330°C (1) alone and (2) as a mixed film with an equal weight of PVC 113.

$\overline{M}_n$ after heating alone	$\overline{M}_n$ after heating with PVC
133,000	45,000
130,000	43,900
	54,000

original $\overline{M}_n$ = 206,000

(b) The effect on the molecular weight ($\overline{M}_n$) of PMMA FRI of being heated (at 5°/min.) to 330°C (1) alone and (2) as a mixed film with an equal weight of PVC 113.

$\overline{M}_n$ after heating alone	$\overline{M}_n$ after heating with PVC
1,405,000	253,000
1,265,000	324,000
1,210,000	337,000

original $\overline{M}_n$ = 1,580,000

(c) The effect of isothermal heating at 190°C on the molecular weight ($\overline{M}_n$) of PMMA anionic (1) alone and (2) as a mixed film with an equal weight of PVC 113.

Time of heating	0	1	2	3	(hours)
Polymer alone	206,000	216,000	224,000	186,000	($\overline{M}_n$)
Polymer + PVC 113.	206,000	190,000	177,000	163,000	($\overline{M}_n$)

extract from mixed samples again being compared with that of pure PMMA which had been heated for the same length of time. These results, shown in table (7,1,C) indicate that even under such mild conditions, PMMA suffers a more rapid molecular weight drop in mixed systems.

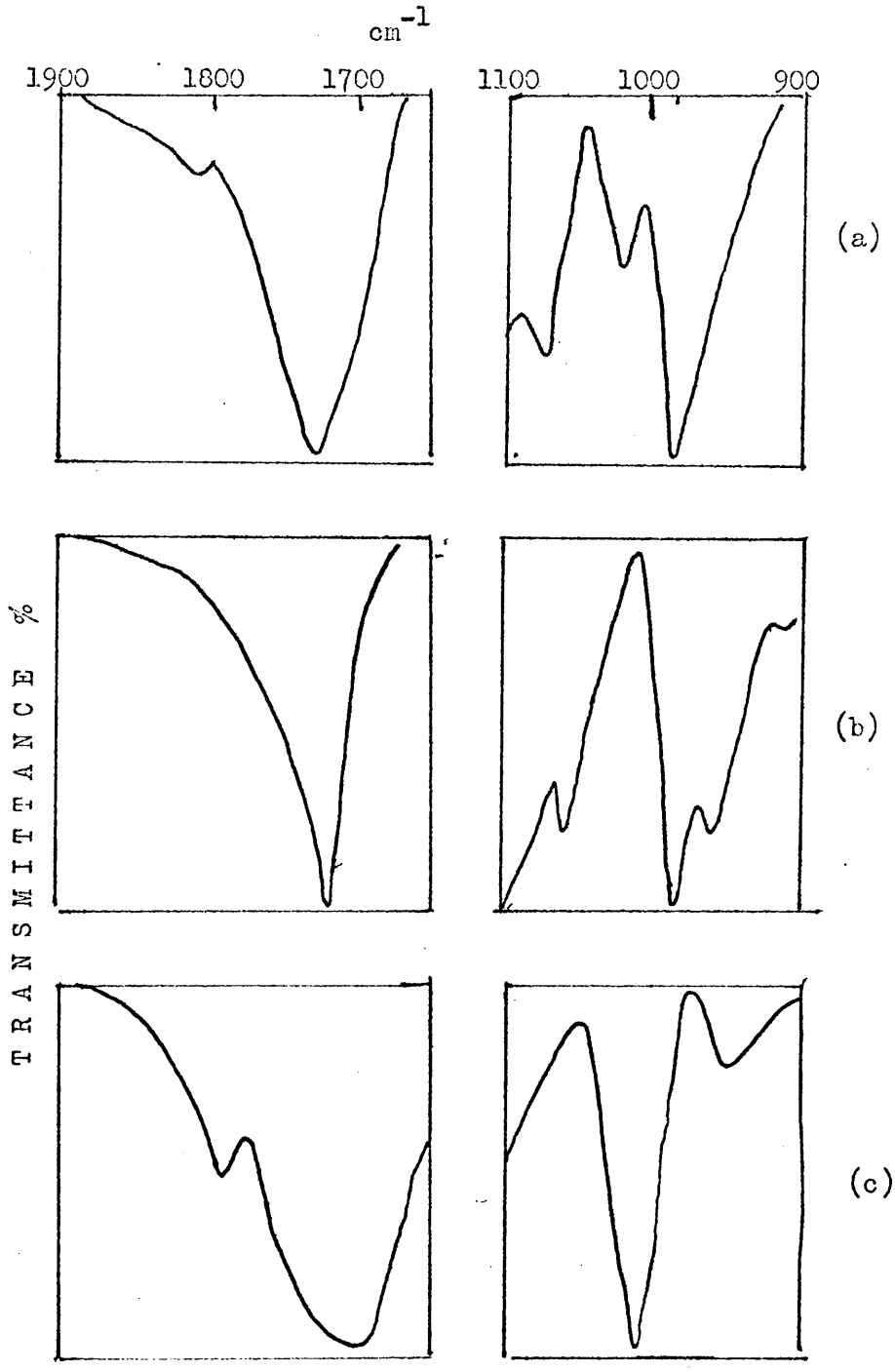
Infra-Red Analysis of Residue.

Mixed Films.

Infra-red spectra were obtained of PMMA films, and PMMA-PVC films before and after degradation. In the case of mixed films, however, the peaks were too broad to permit detection of any changes occurring in the residue. This was probably due to scattering of the incident light beam, caused by the opacity of the mixed film.

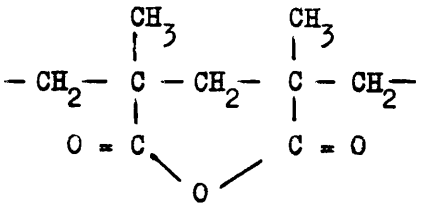
Polymer Removed by Toluene Extraction of Mixed Films.

The toluene extract from a mixed film heated to 330°C was poured into Analar Methanol and the polymer precipitated. The polymer was then dried under vacuum, and an infra-red spectrum obtained (sample as a powder, pressed into a KBr disc), which is shown in figure (7,16 (a)), along with that obtained for PMMA which had been heated alone to the same temperature (figure 7,16 (b)). There is little difference between the two spectra, except that small peaks at 1020 and 1800 cm^{-1} suggest that anhydride units are present, reminiscent of the structures which arise in



Figure(7,16), Infra-red spectra, (powdered polymers, KBr disc) of :-
(a) Toluene extract from PMMA anionic - PVC 113 film which had been heatd to 330°C at 5°/min.
(b) PMMA anionic which had been heated to 330°C at 5°/min.
(c) Poly(methacrylic acid) which had been at 250°C for 90 minutes.

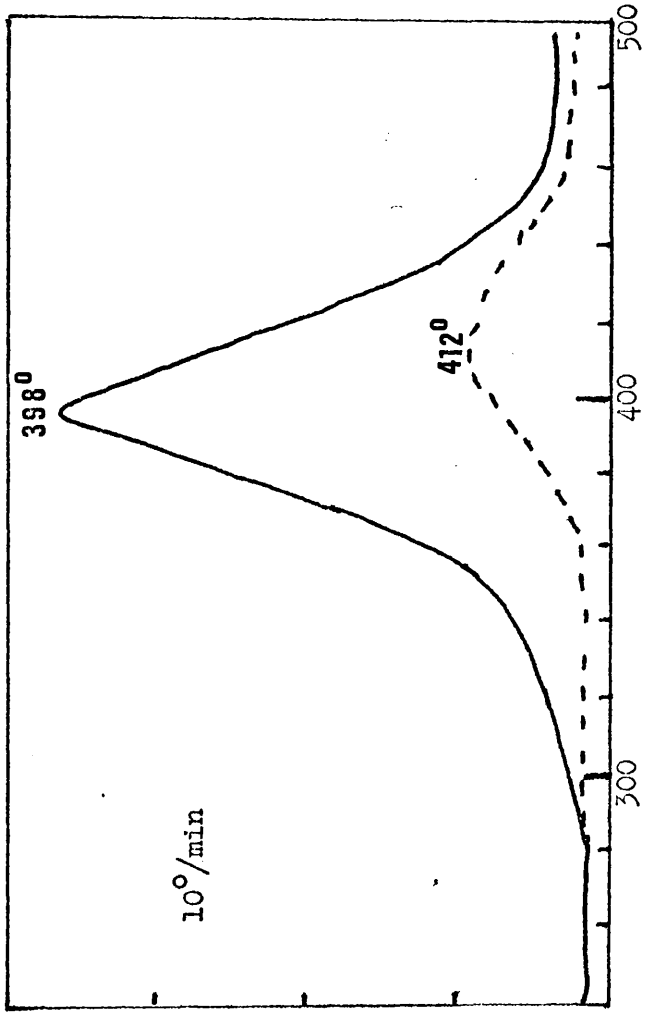
poly (methacrylic acid)on heating[95]:-



Study of Toluene Extract from Mixed Films by TVA.

(a) A small volume of the toluene extract from the residue of degradation to 330°C of a PVC 113 - PMMA anionic film was evaporated to dryness in the degradation tube, and a TVA thermogram obtained, as is shown in figure (7,17). The peak obtained is similar to that for the original PMMA anionic, except that Tmax is displaced to higher temperatures (compare figure (3,14) with (7,17). A Pirani gauge placed beyond a cold trap at - 100°C suggests that unlike PMMA anionic, non condensable material is evolved. It was observed, on examining the degradation tube after degradation of this sample, that a small amount of black residue remained (which is absent on degradation of PMMA).

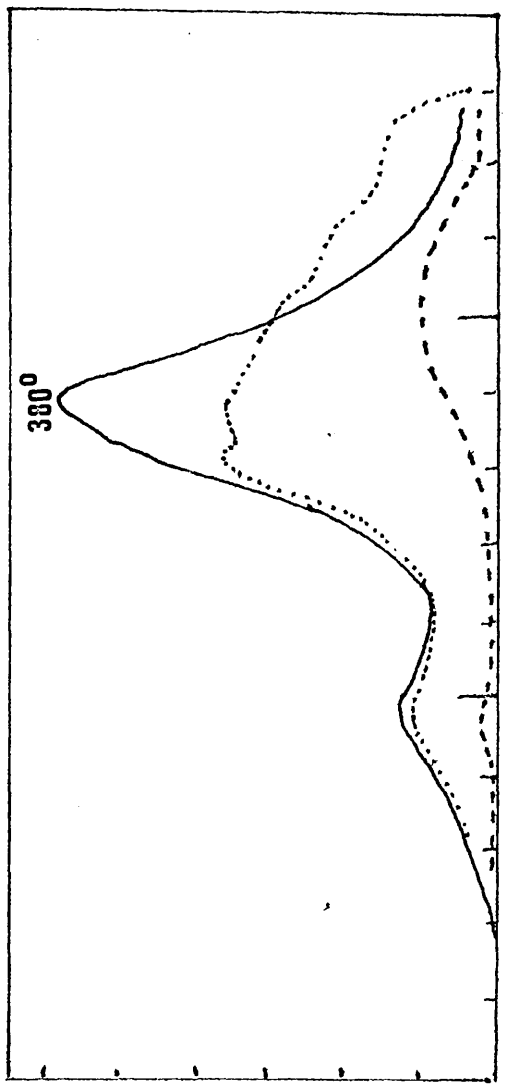
(b) The toluene soluble portion of the residue from an isothermal degradation at 190°C of a mixed film of PMMA anionic-PVC 113 was also subjected to TVA. The DC - TVA thermogram shown in figure (7,18) indicates that the main degradation peak is again displaced to higher temperatures than in PMMA anionic, and



FIGURE(7,17), TVA thermogram of the toluene extract from a PMMA anionic - PVC 113 mixed film which had been heated to 330°C at 5°/min.

———— Output from Pirani gauge placed between sample and cold trap

- - - - - - - - Output from Pirani gauge after a cold trap at -100°C



FIGURE(7,18), DC-TVA thermogram of PMMA anionic which has been heated with PVC 113 at 190°C for one hour, then removed from the polymer blend by toluene extraction.

For key to the representation of Pirani traces, see Figure(6.1).

an additional peak has arisen in the early stages of decomposition, with a maximum at 298°C. Since this peak is associated with the production of a negligible amount of non condensable material, it is confirmed that toluene extraction does not remove PVC from the polymer blend.

The origin of this early peak is not clear. It is possible that the small traces of PVC carried over by toluene extraction are causing the usual type of interaction observed in PVC - PMMA blends. The effect of small amounts of PVC on the thermal stability of PMMA has already been pointed out. Another possible interpretation of the origin of this peak will be given in a later section of this Chapter.

It is evident, however, from this study of the PMMA which has been extracted from the partially degraded blend, that the displacement of the second degradation peak in the mixed film thermogram is almost certainly due to structural changes which occur in the PMMA during the PVC dehydrochlorination process.

INTERPRETATION AND DISCUSSION.

Nature of the Interaction.

Any explanation of the behaviour of PVC - PMMA blends must account for the following facts:-

(a) In the presence of thermally degrading PVC, the molecular

weight of PMMA falls more rapidly than in the pure polymer, under the same conditions.

(b) The early stages of decomposition of mixed films is associated with the production of a greater amount of methyl methacrylate than is produced from the unmixed polymers.

(c) The production of hydrogen chloride, from PVC is delayed in the presence of PMMA.

(d) In the later stages of degradation of mixed films, less volatile material is evolved than from the unmixed polymers, and the rate maximum is displaced to higher temperatures. This appears to be caused by structural changes induced in the PMMA by the dehydrochlorination of PVC.

(e) Anhydride units appear in PMMA which has been heated with PVC.

(f) Methyl chloride is produced in small quantities, from PMMA - PVC blends.

Since no single mechanism can be devised to account for these factors, some attempt will be made to explain each point in turn.

Evidence for Radical Attack on PMMA.

The increased monomer production, and fall in the molecular weight of PMMA in the presence of degrading PVC are

probably related phenomena. The most likely explanation is that PMMA is subjected to a radical attack, by a hydrogen abstraction process. Using the convention adopted in Chapter 1, page (3) we have:-

(1) $PVC \longrightarrow R\cdot$

(2) $R\cdot + M_n \longrightarrow RH + P_n\cdot$ Hydrogen Abstraction.

(3) $P_n\cdot \longrightarrow P_j\cdot + M_{n-j}$ Chain Scission.

(4) $P_j\cdot \longrightarrow P^{\cdot}_{j-1} + M_1$ Depropagation.

Where R· = radical from degrading PVC and M_x and $P^{\cdot}_x$ represent polymer molecules and polymer radicals respectively, X monomer units in length.

The fall in molecular weight is associated with step (3), while step (4) leads to monomer production.

If PVC degrades by a radical mechanism, as is implied by the reaction scheme above, then two types of radical might be capable of participating in step (2), chlorine radicals, or macromolecular radicals:-

$Cl\cdot$ or $-CH{=}CH{-}\overset{\cdot}{C}H{-}CH_2-$

As previously discussed, page (211) any radical species formed during the decomposition of PVC must, in order to react with a PMMA chain, be capable of migrating across a phase boundary. Since the motion of the PVC polymer radical is severely restricted,

it would appear that the more likely attacking species is the chlorine radical. Furthermore, polymer radicals, which ESR spectroscopy has shown are present in dehydrochlorinated PVC (see Chapter 6, page 177) have no effect on PMMA, since the addition of the PVC carbonaceous residue did not lead to increased volatilisation from PMMA (see page 233).

A possible reaction scheme for the attack of chlorine radicals on PMMA is shown in figure (7,19). It is impossible to state with certainty which hydrogen atom in the PMMA chain would be most susceptible to radical attack. The evidence from chlorination experiments [96] is that each of the hydrogens in the chain can be replaced by chlorine. Furthermore, it has been observed that the molecular weight of PMMA falls during chlorination.

Production of radicals A and C, followed by cleavage of the carbon-carbon bond beta to the unpaired electron produces a radical capable of depolymerising, and an unsaturated chain end. Production of radical B, by attack of the ester hydrogen, cannot lead to evolution of monomer directly. It is proposed, however, that B, by intramolecular transfer of hydrogen, can transfer the radical activity so that A or C radicals are produced.

The mechanism can therefore account for the production of monomer, but also predicts that unsaturated molecular chain ends

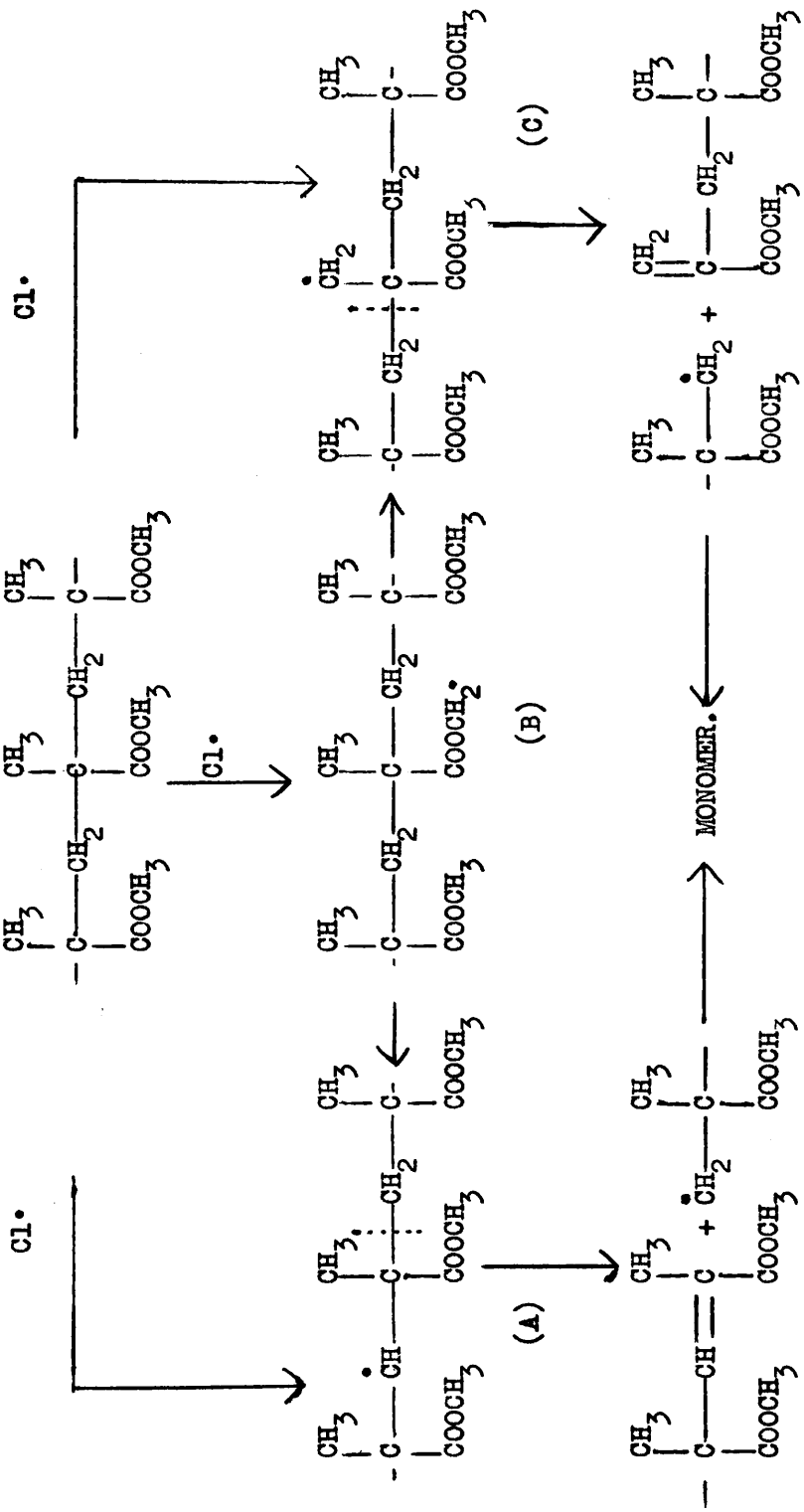


FIGURE (7,19), The effect of chlorine radicals on PMMA.

are produced during the reaction. If so, then these structures should be revealed by TVA, owing to their thermal instability.

The appearance of an additional peak in the TVA thermogram of PMMA anionic which had been extracted from a partially degraded mixed film has already been noted (see page 255). It may be that this peak is due to the presence of such end structures. Certainly the Tmax value is within the range observed for free radically prepared samples of PMMA [6].

Delay in Production of HCl from Mixed Films.

Possibility of Diffusion Control.

A possible interpretation for the delay in the production of HCl from mixed films is that in the presence of PMMA, the escape of HCl is diffusion controlled. However, the fact that relatively small amounts of PMMA are capable of delaying HCl evolution in isothermal experiments argues against diffusion control since the presence of, say 10% PMMA in a PVC film would hardly be expected to impose a diffusion controlled reaction on the decomposition of the film. Also, if the escape of monomer from PMMA is not diffusion controlled, as is indicated by the results of Chapter 3, it seems unlikely that the small HCl molecule would experience much delay on this account.

Possibility of Reaction between HCl and PMMA.

It will be shown in a subsequent section of this Chapter that

there is evidence to suggest that HCl reacts with PMMA in mixed films. It is possible that it is this secondary reaction which causes the delay in HCl production, rather than the passive retention of HCl by the second polymer. However, HCl production from PVC - polyisobutene blends is also delayed, and it seems unlikely that any reaction between HCl and the second polymer can occur in this case.

Possibility of Added Polymer Acting as an Inhibitor.

The reaction scheme shown in figure (7,19) gives rise to an alternative explanation.

Chlorine radicals which react with PMMA will not be available to initiate dehydrochlorination in PVC. In other words, the second polymer may be competing with PVC for chlorine radicals, acting as a rather inefficient radical scavenger for chlorine radicals:-

$$Cl\bullet + PH \longrightarrow HCl + P\bullet$$

$$P\bullet \longrightarrow \text{secondary reactions.}$$

If this interpretation is correct, then it would be expected that any polymer containing hydrogen atoms which are capable of abstraction by chlorine radicals, would inhibit the dehydrochlorination of PVC. Experiments on PVC blends with a variety of other polymers (see page 271) suggest that the delay in production of HCl from mixed films is indeed a general phenomenon.

Displacement of Main PMMA Degradation Peak.

As previously stated, (page 252), structural changes occur in PMMA, as a result of heating with PVC, which cause the main PMMA degradation peak to be displaced in higher temperatures, in mixed films. Two possible interpretations of this phenomenon can be advanced at this stage:-

(a) Influence of Molecular Weight.

McNeill has shown that the TVA thermogram of PMMA samples is strongly dependent on the molecular weight of the polymer used. The Tmax for the main degradation peak is lower, for samples of higher molecular weight. As previously stated (see page 248), the molecular weight of PMMA falls during the dehydrochlorination of PVC, and the displacement of the peak to higher temperatures in mixed films can be attributed to this molecular weight decrease. The fact that less volatile material is evolved from mixed films in this temperature range is probably due to the PVC induced degradation which occurs in the earlier stages of reaction, and results in there being less PMMA available for degradation after dehydrochlorination of PVC is completed.

(b) Effect of Anhydride Units.

Infra-red spectra of the residue indicate that anhydride units arise in PMMA which has been heated with PVC. Whatever their

mode of formation, these ring structures could be the reason for the displacement of the PMMA degradation peak, by reducing the efficiency for monomer production from the PMMA chain. The anhydride rings, in acting as blocking units towards the depolymerisation of the polymer chain, would cause the displacement of Tmax in the same direction as would be caused by a molecular weight drop, in an analogous way to the reduction of the kinetic chain length of depolymerisation by the lactone rings in MMA - VC copolymers (see pages 199 to 201).

The presence of small amounts of carbon dioxide in the degradation products of mixed films, as suggested by infra-red analysis of the products, can be attributed to the thermal decomposition of anhydride units. The production of carbon dioxide is probably the cause of the non condensable peak in the presence of PVC (see page 252 and figures 7,17 and 7,18).

Confirmation that carbon dioxide is evolved during the decomposition of anhydride units comes from the product analysis of the decomposition products of poly (methacrylic anhydride). When an infra-red gas cell spectrum was obtained of the products of degradation of this polymer, in a closed system of the type shown in figure (5, 11), a strong peak for carbon dioxide was observed, together with peaks suggesting the presence of carbon

monoxide and methane. The absence of the latter compounds in the products obtained from mixed films is almost certainly due to the fact that they are not condensable by a cold trap at liquid nitrogen temperature.

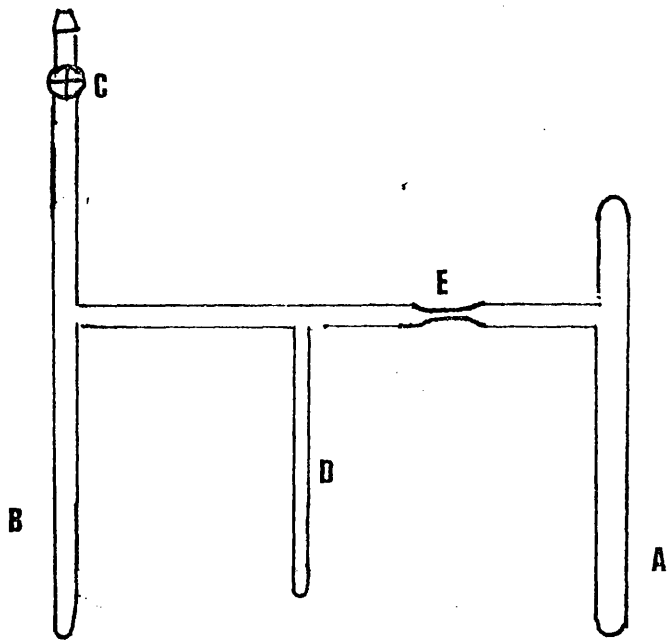
Production of Anhydride Units.

The most probable cause of the formation of anhydride units in PMMA which has been heated with PVC is the attack of the PMMA chain by HCl.

To test this assertion, a sample of PMMA anionic was heated for 24 hours in the presence of gaseous hydrogen chloride. The simple glass apparatus, shown in figure (7,20) was used for this purpose.

100 mg. of PVC 113 was placed in limb A, and 100 mg. of PMMA anionic placed in B. The system was then evacuated through C. Once the vacuum was satisfactory, C was closed, and A was heated to 500°C, with a liquid nitrogen trap at D. D was allowed to cool, and the apparatus was sealed off at the constriction E. Limb B was then heated isothermally for 12 hours, at 190°C, in a TVA oven, with no cold trap around D.

As a result of this treatment, the PMMA was rendered insoluble, and could not be powdered. An infra-red spectrum could therefore not be run. The residue was investigated by



FIGURE(7,20), Apparatus for testing the effect of hydrogen chloride gas on the structure of PMMA.

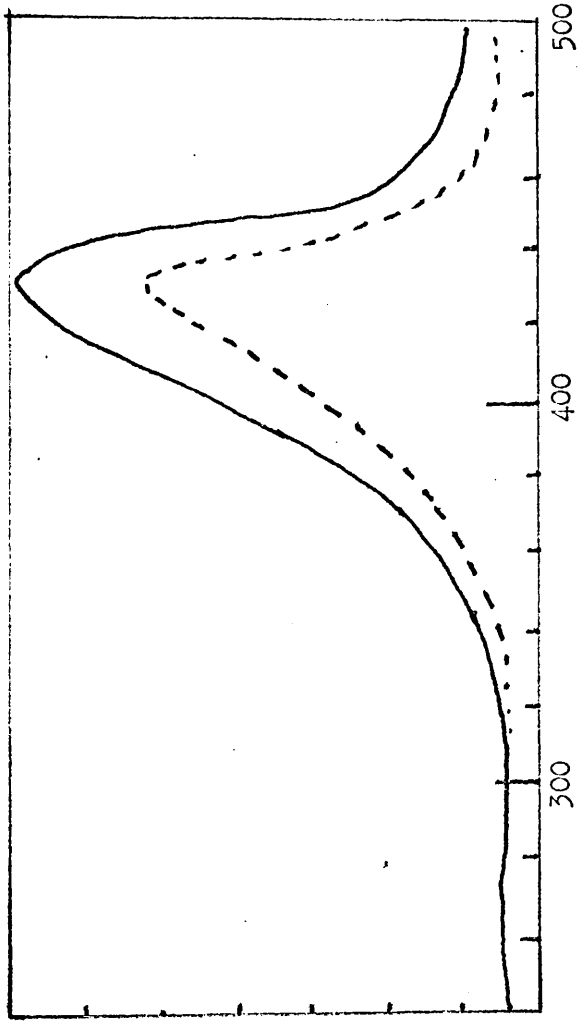
TVA, and the thermogram is shown in figure (7,21). It was noted that the polymer left a black residue, at the end of the TVA experiment.

Clearly, the TVA thermogram of the polymer indicates that the HCl treatment had altered the structure of the PMMA, so that the main degradation peak was displaced to higher temperatures, and, as in the case of poly (methacrylic anhydride), the volatile products were not fully condensed at - 100°C (carbon dioxide, carbon monoxide, methane).

It appears, therefore, that anhydrous HCl (from PVC) is capable of causing the formation of anhydride units in PMMA.

Further evidence that HCl can react with PMMA in this manner comes from the work of McNeill and Gardner [97], in a study of the TVA thermograms of mixed, and unmixed samples of polychloroprene and PMMA. Since the principal volatile product of thermal degradation of polychloroprene is hydrogen chloride, it might be expected that the two polymers would interact in a similar fashion to the PVC - PMMA system.

The mixed polymers do interact on degradation, the main degradation peak for PMMA being displaced to higher temperatures in the presence of polychloroprene, and carbon dioxide is evolved from the blend, suggesting that HCl from degrading polychloroprene



FIGURE(7,21), TVA thermogram of PMMA anionic which has been heated at 190°C in an atmosphere consisting of the products of degradation of PVC 113.

For key to the representation of Pirani traces, see Figure(7,17).

has attacked the PMMA chain, again producing anhydride units, which decompose to produce carbon dioxide.

However, in the early stages of decomposition of polychloroprene - PMMA blends, the rate of volatilisation is reduced, rather than increased. This is in contrast to the situation in PVC - PMMA blends, where even small quantities of added PVC are capable of significantly reducing the stability of PMMA.

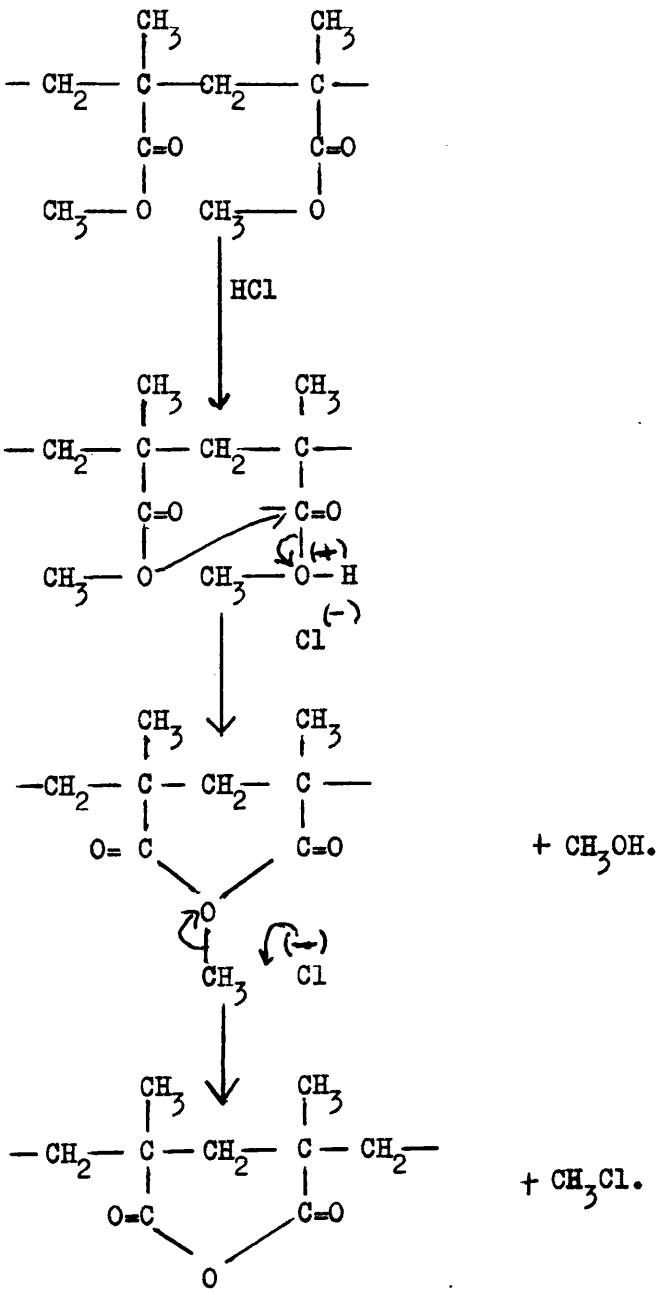
It would therefore appear that the increased volatilisation in the early stages of the breakdown of PVC - PMMA blends is not caused by the reaction between HCl and the PMMA, but is due to radical attack, as previously suggested.

A possible mechanism for the reaction between HCl and PMMA is shown in figure (7,22). This suggests that for each anhydride unit formed, molecules of methyl chloride, and methanol are produced. Although the presence of the former substance was indicated by mass spectrometry, no methanol was detected by any of the techniques used to analyse the products, nor was it reported by Zutty and Welch [85], or Barlow, Lehrle and Robb [25]. A possible explanation is that any methanol produced reacts with HCl to give methyl chloride.

The fact that methyl chloride was not detected by infra

FIGURE 7,22.

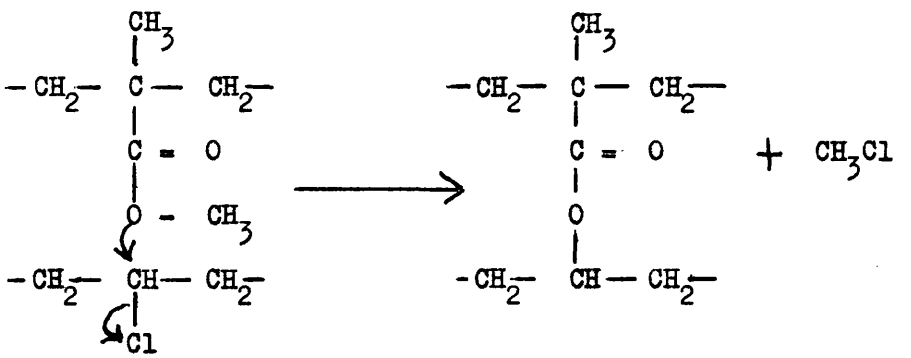
POSSIBLE EFFECT OF HCl on PMMA.



red analysis is probably due to the low yields of this compound from the mixed system, as indicated by Zutty and Welch [85].

Production of Methyl Chloride - Alternative Mechanism.

It may be that some methyl chloride can be produced by a reaction analogous to that which occurs in VC - MMA copolymers, although in this case the process would involve the intermolecular condensation between unlike chains:-



For the reasons discussed earlier, this reaction could only occur at phase boundaries within the mixed polymer system, since close approach is required between unlike molecules.

Furthermore, a cross linking reaction of the type described above, would cause the molecular weight of the residue to increase, in contrast to the observed fall in molecular weight which occurs in the polymer blend. It is almost certain therefore, that this process is not an important reaction in polymer blends, and that methyl chloride is formed predominantly as a result of the reaction between HCl and PMMA.

The formation of methyl chloride, whether it is associated with the production of anhydride rings, or the formation of interchain bonds, cannot be the cause of the increased volatilisation

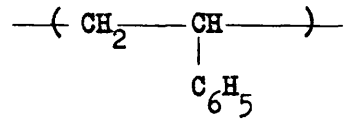
in the early stages of the degradation of the mixed polymers, since the studies of the MMA - VC copolymer system clearly established that methyl chloride is not condensed by a cold trap at - 100°C.

OTHER POLYMER BLENDS CONTAINING PVC.

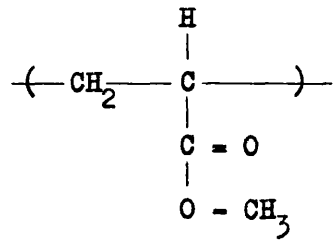
It is of interest to compare the behaviour of PVC - PMMA blends with that of other polymer blends containing PVC.

In figures (7,23) to (7,26) are shown the TVA thermograms, obtained at a heating rate of 5°/min in each case [98], for the following systems, in mixed and unmixed conditions:-

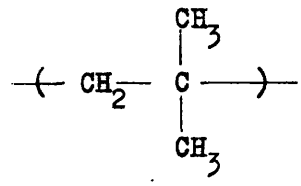
PVC 113 - Polystyrene



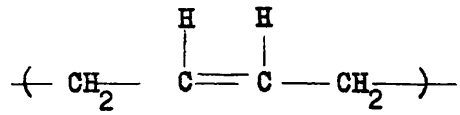
PVC 113 - Poly (methyl acrylate)



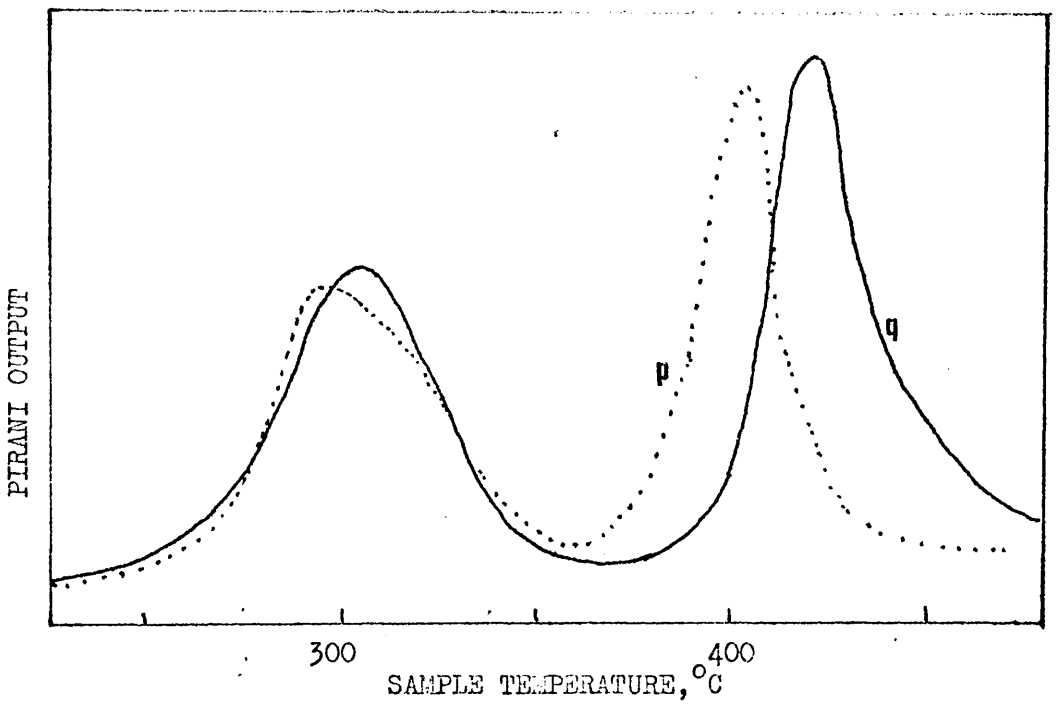
PVC 113 - Polyisobutene



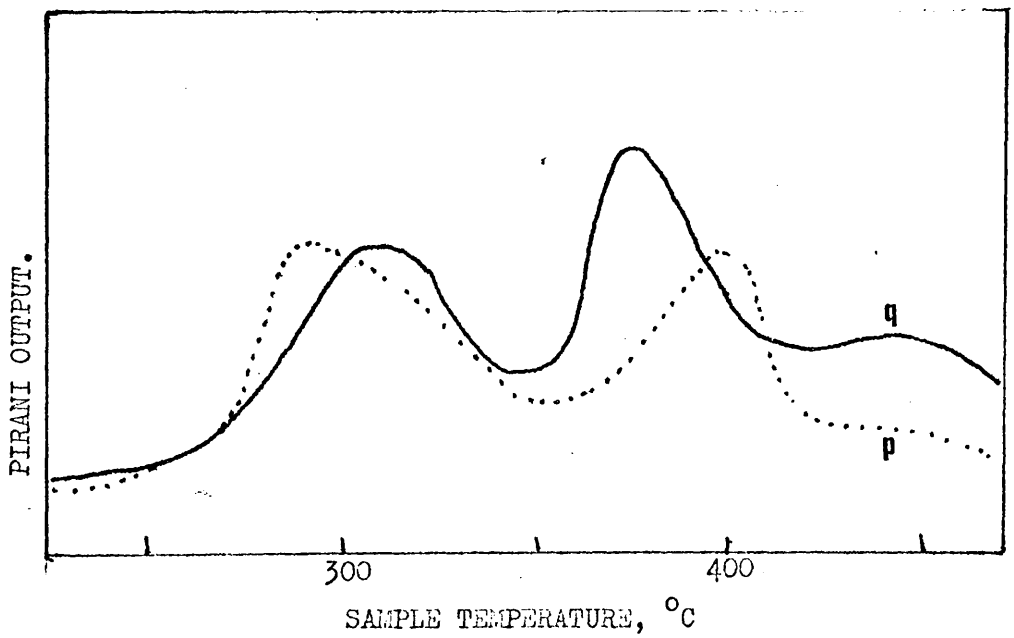
PVC 113 - cis - Polybutadiene



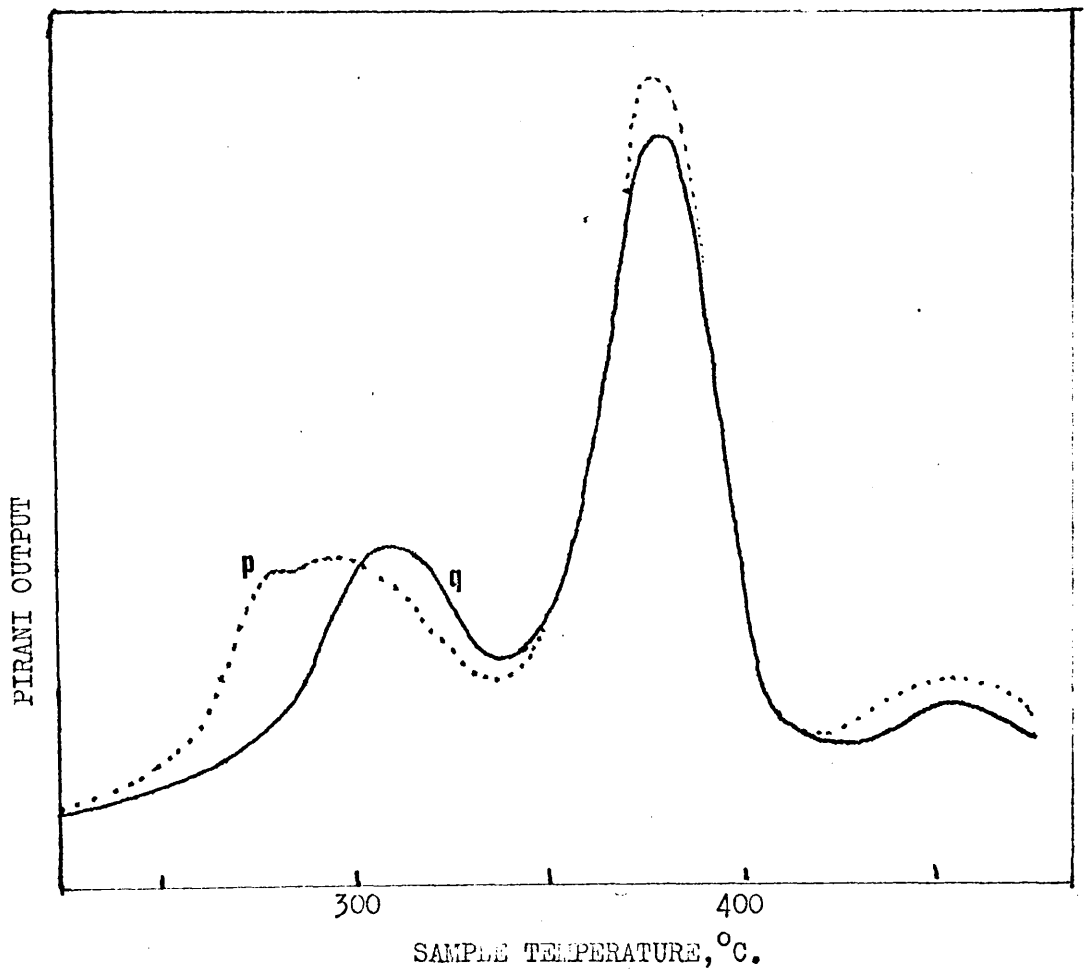
The origin of the polymers is detailed in Appendix I, and in each case the samples were prepared for degradation as films,



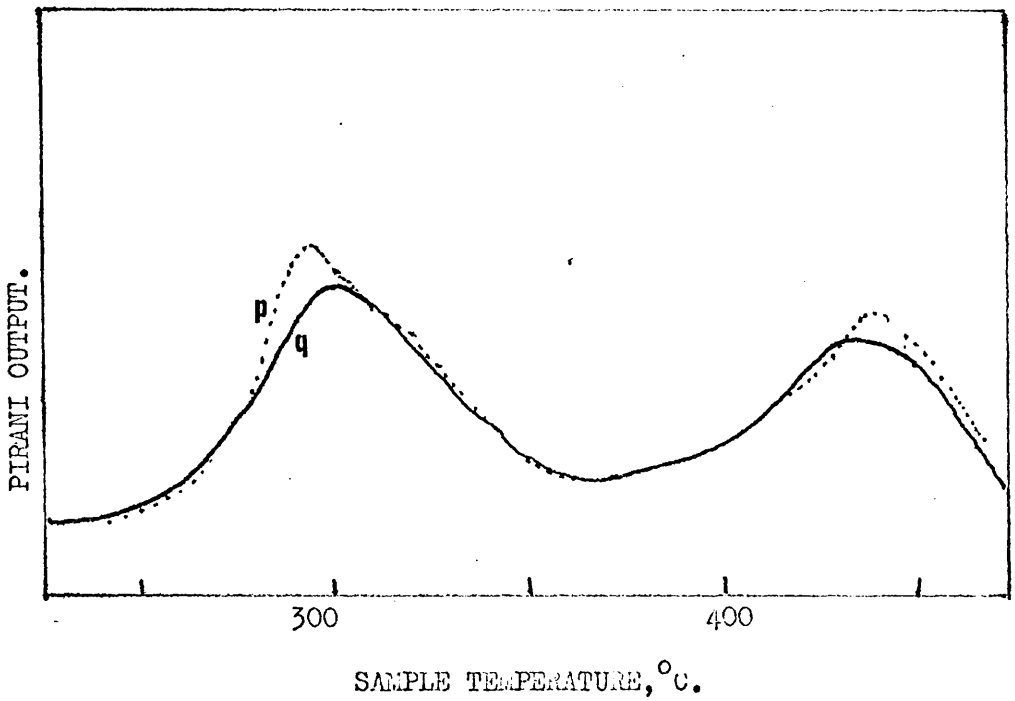
FIGURE(7,23) TVA thermograms (at 5°/min.) for polystyrene ~~Cat.~~ I.C. and PVC 113. 10mg of each polymer were used. Trace p : simultaneous degradation of unmixed polymers as separate films. Trace q : degradation of films with mixed polymers.



FIGURE(7,24), TVA thermograms for PVC 113 and poly(methyl acrylate) Other details as given in caption for Figure(7,23).



FIGURE(7,25), Tva thermograms for PVC 113 and polyisobutene.
Other details as given in caption for Figure(7,23).



FIGURE(7,26), TVA thermograms for PVC 113 and polybutadiene. Other details as given in caption for Figure(7,23).

cast from cyclohexanone.

Unfortunately it was not possible to study these systems in as much detail as the PMMA - PVC system, so that discussion is limited to the implications of the various thermograms, in the light of the known properties of PMMA - PVC blends.

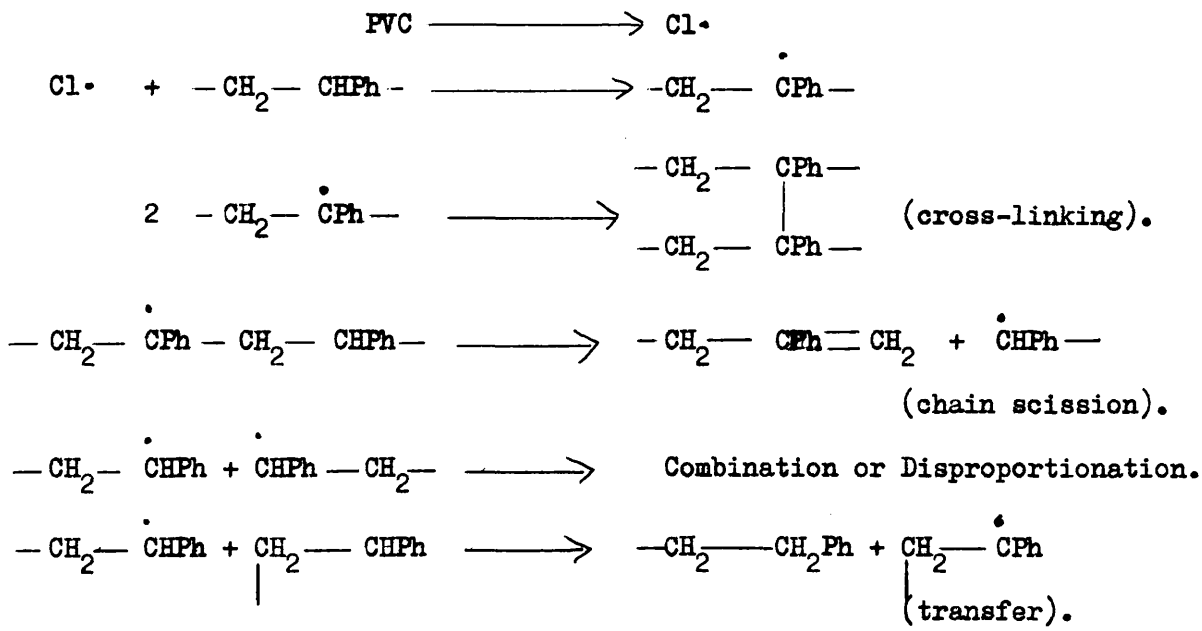
PVC - Polystyrene.

It is clear from the thermograms for unmixed and mixed systems, that there is some form of interaction between the two degrading polymers. The evolution of hydrogen chloride from mixed films (first peak) is slightly delayed, and the degradation peak for polystyrene (second peak) is displaced to higher temperatures in mixed systems. However, unlike PVC - PMMA, there is no noticeable increase in the production of volatile material in the early stages of decomposition of mixed films.

If chlorine radicals, arising during PVC degradation, are capable of attacking polystyrene, then it might have been expected that the polystyrene radical so produced would have given rise to increased yields of monomer, in the same manner as PMMA radicals.

However, there is evidence from the work of Grant and Grassie [99], and McNeill [6], in studies of copolymers containing styrene units, that polystyryl radicals, when produced below 300°C, do not depolymerise until the temperature of breakdown of polystyrene

itself is reached. Presumably the reaction scheme shown below would occur:-



Thus it would be expected that cross linking, or chain scission of the polystyrene would result from the radical attack.

The displacement of the polystyrene degradation peak in the thermogram for the mixed polymers could be a reflection of these radical induced structural changes in the polystyrene. Certainly McNeill and Mohammed [67] have shown that over a wide range of molecular weight, the Tmax values for polystyrene samples are somewhat higher, the lower the molecular weight of the starting material.

The TVA thermograms for PVC - Polystyrene blends are therefore not inconsistent with a radical mechanism for PVC breakdown.

PVC - Poly (methyl acrylate)

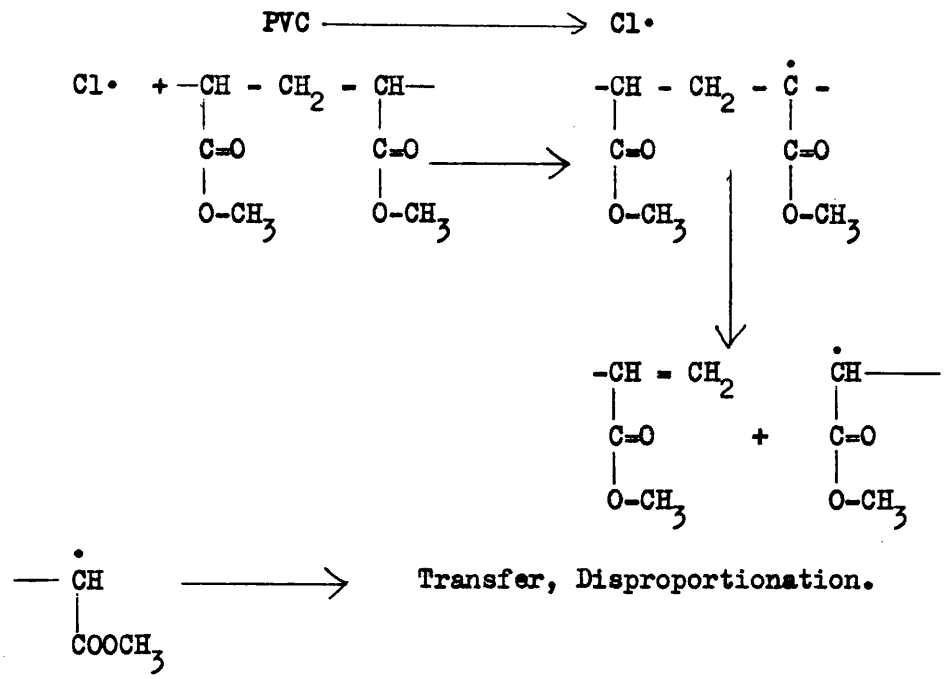
Again, there is clear indication of an interaction between this polymer pair, in mixed films.

There is a delay in the production of HCl from the mixed polymers. However, the second peak, corresponding to the decomposition of poly (methyl acrylate), appears at lower temperatures in the mixed films. This is clearly in contrast to the situation in PVC - PMMA, and PVC - PSt blends.

The reason for this difference almost certainly lies in the different mode of decomposition of the polymers concerned. While both PMMA and polystyrene give high yields of monomer, the decomposition of poly (methyl acrylate) involves low monomer yields, and is believed to involve random scission of the polymer backbone, resulting in a rapid fall in molecular weight, and the eventual production of low polymer [99]. The main volatile products are carbon dioxide and methanol, and mechanisms, involving radical intermediates, have been proposed for the formation of these compounds[100].

The attack by chlorine radicals on the acrylate chain

presumably causes a fall in the molecular weight of the polymer, and probably the production of unsaturated end structures:-



Unfortunately it is not known if the TVA thermogram of poly (methyl acrylate) is dependent upon molecular weight. The results of Cameron and Kane, however, suggest that the molecular weight of the polymer is not crucial.

In the absence of further information therefore, the behaviour of this system cannot be completely explained.

PVC - Polyisobutene.

The most notable feature of the thermogram for the mixed polymers is the delay in evolution of hydrogen chloride, reflected

in a shift in Tmax for the first peak by 10^{o}. The peak at higher temperatures, due to the breakdown of polyisobutene, is unchanged in the mixed system. If, as suggested for PVC - PMMA blends, the delay in production of HCl is due to added polymer causing genuine inhibition of dehydrochlorination by competing with PVC for chlorine radicals, then one would expect the molecular weight of the polyisobutene to fall as a result of the radical attack.

McNeill and McGuchan (101) have studied the TVA thermograms of polyisobutene samples of various molecular weights, and found that the Tmax of the thermogram was independent of molecular weight. Thus one would not anticipate any change in the position of the polyisobutene peak in mixed samples.

PVC - cis Polybutadiene.

In the case of this polymer pair, the only difference between mixed and unmixed systems is a slight delay in the production of HCl in mixed films. Unfortunately not enough is known about the effect of molecular weight on the thermogram of polybutadiene to state whether any molecular weight changes which might be occurring in mixed films, would be reflected in a Tmax change.

A similar apparent lack of interaction was also noted in the case of the PVC - cis polyisoprene system.

CONCLUSIONS.

The study of the PVC - Polystyrene and PVC - Poly(methyl acrylate) systems confirms that the PVC - PMMA system is not unique in exhibiting interaction between the degrading polymers, and shows clearly that unlike polymers can interact during decomposition, even when the polymer pair are incompatible.

It appears to be a common feature of polymer blends containing PVC, that the evolution of hydrogen chloride is delayed. Although this may be caused by diffusion effects, or reaction of hydrogen chloride with the added polymer, the alternative explanation of the second polymer acting as a genuine inhibitor must also be given credence, and is certainly consistent with the observed molecular weight drop of PMMA in the presence of PVC. Furthermore, it is difficult to conceive of a reaction between HCl and polyisobutene which would be capable of delaying the evolution of HCl from this mixed system.

The fall in molecular weight of PMMA in the presence of degrading PVC, and the increased production of monomer from mixed films are clear evidence of the presence of radicals in degrading PVC. The interaction between PVC and polystyrene can also be interpreted on this basis. In the PVC - poly (methyl acrylate) and PVC - polyisobutene systems, further evidence is necessary

before any firm conclusions can be drawn. In each of these cases it would be of interest to observe if heating the polymer in the presence of PVC caused a fall in molecular weight.

Since the behaviour of the PVC - PMMA system suggests that PVC degrades by a radical mechanism, it would appear that renewed interest should be taken in the effect of radical scavengers on the rate of dehydrochlorination of PVC.

A recent publication by Burnett, Haldon and Hay [102] suggests that poly (vinylidene chloride) degrades by a radical mechanism, so it would appear that a study of blends of this polymer, with PMMA, would be of interest.

SUMMARY.

Studies have been carried out using TVA on the thermal degradation of PMMA - PVC blends. It has been found that the mixed polymers are more stable than random copolymers of vinyl chloride and methyl methacrylate, although less stable than the unmixed polymers.

The instability of PMMA in the presence of PVC has been shown to be consistent with the presence of radicals in thermally degrading PVC.

Studies of blends of PVC with other vinyl polymers show that PVC can interact with polymers other than PMMA, possibly by a similar mechanism to that proposed for the PVC - PMMA system.

APPENDIX ONE.

DETAILS OF PREPARATION AND CHARACTERISATION OF POLYMERS USED IN THIS THESIS.

Molecular Weights.

Number average molecular weights were determined using a Mechrolab Model 501 Membrane Osmometer, at 25°C. The membrane and solvent system used in each case are noted in the appropriate sections below.

POLYMETHYL METHACRYLATE. (PMMA).

Methyl methacrylate (I.C.I. Ltd.) was washed with alkali to remove inhibitor, then several times with distilled water, and dried using calcium hydride, or calcium chloride. It was distilled three times in vacuo, only the "middle fraction" being retained from each distillation. Monomer obtained in this way was used to make the PMMA samples used in this work.

PMMA D.F., PMMA I.C., PMMA F.R.I. were obtained from bulk polymerisation at 60°C (in vacuum sealed dilatometer) of purified MMA, with varying amounts of azobisisobutyronitrile, to less than 10% conversion. Polymer was isolated by precipitation with Analar Methanol, and purified by several reprecipitations from benzene solution, and dried under vacuum at room temperature for several days. PMMA A.G. was prepared in an analogous way, except that

benzoyl peroxide was the catalyst used. PMMA anionic was prepared as follows:-

Oxygen was removed from 500 ml of sodium dried Analar toluene by bubbling a steady stream of nitrogen (less than 6 p.p.m. oxygen) through it for two hours. 10 ml of a dry ether solution, containing .024 eq. of freshly prepared phenyl magnesium bromide was added, and the reaction flask placed in an ice bath. 32 ml of purified MMA was then added, dropwise, under continuous stirring, the flow of nitrogen being maintained. Polymerisation was allowed to proceed overnight at $0^{\circ}C$, a slow stream of nitrogen being passed over the surface of the solution, which was continuously stirred. The polymer was isolated by precipitation in petroleum ether, and was washed with a solution containing 1.7 litres water, 300 ml methanol, and a little dilute hydrochloric acid (to remove magnesium salts). The polymer was then washed several times with water, and dried at $60^{\circ}C$ in vacuo. Polymer thus prepared was extracted with toluene at room temperature, filtered, and any insoluble material discarded. The polymer was purified by precipitation in methanol (three times), and dried for several days at $40^{\circ}C$ in vacuo. The yield was 10g.

The $\overline{M}n$ values for the PMMA samples, (toluene solution, osmometer fitted with Sylvania 300 grade cellophane membrane) were:-

PMMA D.F.	421,000.
PMMA I.C.	134,000.
PMMA F.R.I.	1,580,000.
PMMA A.G.	905,000.
PMMA Anionic.	206,000.

POLYSTYRENE. Monomer was purified in a similar way to that described for MMA. Polystyrene Cat. was prepared by S. Haider at -78°C, using stannic chloride as a catalyst. Polystyrene I.C. was prepared by I. Cooke by bulk polymerisation at 60°C using azobisisobutyronitrile as catalyst. NBS 706 was a National Bureau of Standards sample. The quoted conditions of preparation being, "thermal polymerisation at 140°C to 37% conversion".

The $\overline{M}n$ values for polystyrene samples (toluene solution, osmometer fitted with Sylvania 300 grade cellophane membrane), were:-

Polystyrene Cat.	108,000.
Polystyrene I.C.	228,000.
Polystyrene NBS 706.	136,000.

POLY (METHYL VINYL KETONE) and POLY (METHYL ISOPROPENYL KETONE).

MVK and MIK (Bisol Ltd.) were purified as for MMA, the drying agent being anhydrous magnesium sulphate, and distilled under nitrogen until the infra-red spectrum of each monomer was the same as a reference spectrum [62]. Monomer so obtained was thrice

distilled in vacuo, before polymerisation. PMVK A was prepared by polymerising MVK in bulk at 60°C with 0.1% W/V azobisisobutyronitrile, PMVK B at 40°C with 0.1% initiator, PMVK D at 40°C with 1% initiator. PMIK E was prepared by polymerising MIK at 40°C with 1% initiator and PMIK F at 60°C with 1% initiator. PMIK Fort. was prepared by fortuitous polymerisation at room temperature of the impure monomer. In each case polymers were isolated by precipitation in methanol, and purified by repeated precipitation from acetone/methanol.

Molecular weights ($\bar{M}n$) were determined in methyl ethyl ketone solution, using Sylvania 300 grade cellophane membrane.

PMVK A,	132,000.
PMVK B.	401,000.
PMVK D.	362,000.
PMIK E.	70,500.
PMIK F.	59,100.
PMIK Fort.	220,000.

MMA - VC copolymers.

A measured volume of MMA (purified) was distilled into a dilatometer containing a known weight of benzoyl peroxide. Vinyl chloride (I.C.I. Ltd.,) was distilled from the cylinder into a suitable reservoir and degassed, before distillation into the dilatometer.

Polymerisations at 60°C were carried to less than 5%, and the copolymers obtained had the compositions detailed in figures (6,3) to (6,7), which were calculated using the reactivity ratios of Mayo [86].

PVC. PVC A.G. was prepared by polymerisation at 60°C of vacuum distilled VC, using 0.35 weight % benzoyl peroxide. PVC 113, PVC 121, PVC 101 and PVC 121 were British Geon samples, stated to be free from impurities. The polymer most used in this work (PVC 113) was stated to have a molecular weight (determined by viscosity measurements), of 45,600. It was found to have $\overline{M}n$ = 64,500 (in ethyl benzoate solution, using an Ultracellafinter "allerfeinst" membrane). Before use in the experiments detailed in Chapter 7, the PVC 113 was purified by precipitation into methanol from cyclohexanone solution, and dried in vacuo at 40°C for several days. It was then extracted with "Analar" toluene (three times, at 40°C, the soluble fractions being discarded). The polymer was filtered, washed with toluene, and dried as before. PVC 176 A was a low molecular weight sample, donated by Dr. Bengough ($\overline{M}n$ = 7,000), and had been prepared at 60°C using benzoyl peroxide as catalyst.

Polyisobutene was prepared by R. McGuchan, at - 78°C, using stannic chloride as initiator. $\overline{M}n$ was 100,000.

Poly (methyl acrylate) was prepared at 60°C by A.W. McAllister from a 20% solution of the monomer in n-propyl acetate using 0.1% W/V azobisisobutyronitrile as catalyst. $\overline{Mn}$ was 684,000.

Polybutadiene and cis - polyisoprene were industrial samples, kindly supplied by the India Tyre and Rubber Co. Both polymers were purified before use, the former by precipitation in Analar acetone from n-hexane solution.

APPENDIX TWO COMPUTER PROGRAMME

This programme calculates the value of - -dw/dt every int degrees, between the temperature limits Ti and Tf, for a first order reaction,for given values of A, E, and B,

where A = pre-exponential factor,

E = energy of activation,

B = heating rate,

Ti= temperature at which calculation begins,

Tf= temperature at which calculation ends,

The programme is as follows :-

```
begin integer i, fa, fb;
      real W, A, R, E, B, Ti, Tf, T, int, y, Q;
      open(7C); open(2C);
      title: i:= in basic symbol (2C);
      if i= 152 then goto out else out basic symbol (7C,i);
      goto title;
out: W:=read(2C); A:=read(2C); R:=read(2C); E:=read(2C);
        B:=read(2C);
```

(continued on following page)

```
write text (7C, [[cc] COLUMNS*ARE*T*AND*-dW/dt[cc]]);
Ti := read(2C);  Tf := read(2C);  int := read(2C);
fa := format ([sss-ndddd.dd]);
  fb := format([ssssss-d.ddddd10+ndcc]);
for T := Ti step int until Tf do
 begin  Q := R × T↑2 × exp( -E/( R×T )) / E;
        y  := A × W × exp( -E/( R×T ) - (A × Q / B));
        write (7C, fa, T);  write (7C, fb, y);
 end;

 close(7C);   close(2C);
 end→
```

REFERENCES.

1. N. Grassie, "Cleavage Reactions - Thermal Degradation", in "Chemical Reactions of Polymers", E.M. Fettes (ed.)., Interscience (1964), page 566.
2. L.A. Wall, S.L. Madorsky, D.W. Brown, S. Straus and R. Simha, J. Amer. Chem. Soc., 76, 3430 (1954).
3. N. Grassie and H.W. Melville, Proc. Roy. Soc. (London), A199, 1; 14; 24; 39; (1949).
4. R. Simha, L.A. Wall and P.J. Blatz, J. Polymer Sci. 5, 615, (1950).
5. J.R. MacCallum, Makromol Chem., 83, 137 (1965).
6. I.C. McNeill, Europ. Polym. J., 4, 21 (1968).
7. Reference 1, pages 574 - 576.
8. Reference 1, pages 569 - 573.
9. P.M. Sykes, Mechanism in Organic Chemistry, Longmans (1961).
10. Reference 1, page 571.
11. G.C. Marks, J.L. Benton and C.M. Thomas, S.C.I. Monograph No. 26, London (1967), p. 204.
12. D. Druesdow and C.F. Gibbs. Nat. Bur. Stand. Circ. 525 (1953), 69.
13. R.R. Stromberg, S. Straus and B.G. Achhammer, J. Polymer Sci., 35, 355 (1959).
14. D.H. Grant and N. Grassie, Polymer 1, 445 (1960).
15. N. Grassie and J.N. Hay, J. Polymer Sci., 56, 189 (1962).

16. N. Grassie and J.N. Hay, S.C.I. Monograph No. 13, London 1961.

17. D.H. Grant and N. Grassie, Polymer 1, 125 (1960).

18. J.N. Hay and N. Grassie, Makromol. Chem., 64, 82 (1963).

19. D. Dollimore and G.R. Heal, Carbon, 5, 65 (1967).

20. W.C. Geddes, Europ. Polymer J., 3, 747 (1967).

21. N. Grassie and I.C. McNeill, J. Polymer Sci., 30, 37 (1958).

22. W.C. Geddes, Europ. Polymer J., 3, 733, (1967).

23. N. Grassie and I.C. McNeill, J. Polymer Sci., 27, 207, (1958).

24. G.M. Burnett, R.A. Haldon and J.N. Hay, Europ. Polymer J., 4, 83 (1968).

25. A. Barlow, R.S. Lehrle and J.C. Robb, S.C.I. Monograph 17 (London), 267, (1963).

26. D.A. Vassallo, Anal. Chem., 33, 1823, (1961).

27. D. Smith, Nature, 208, 1200 (1965).

28. C.E.R. Jones and A.F. Moyles, Nature, 191, 663 (1961).

29. E.E. Lewis and M.A. Naylor, J. Amer. Chem. Soc., 69, 1968, (1947).

30. S.L. Madorsky, S.P.E.J. 17, 665 (1961).

31. S. Straus and S.L. Madorsky, J. Res. Nat. Bur. Stand., 66A, 401 (1962).

32. F.A. Lehmann and G.M. Brauer, Anal. Chem., 33, 673 (1961).

33. I.C. McNeill, Europ. Polymer J., 3, 409 (1967).

34. G.M. Lukaszewski, Nature, 194, 959 (1962).

35. S.L. Madorsky, V.E. Hart, S. Straus and V.A. Sedlak, J. Res. Nat. Bur. Stand., 51, 327 (1953).

36. W.W. Wendlandt, Thermal Methods of Analysis, Interscience, Chapter 3, (1964).

37. H.C. Anderson, in Techniques and Methods of Polymer Evaluation, Volume 1 - Thermal Analysis, Slade and Jenkins, eds., Arnold, (1966), page 111.

38. J.H. Flynn and L.A. Wall, J. Res. Nat. Bur. Stand., A 70A, 487 (1966).

39. S. Gordon and C. Campbell, Anal. Chem., 32, 271R (1960).

40. Reference 36, page 20.

41. Reference 37, C.D. Doyle, pages 114 - 120.

42. Reference 36, page 207.

43. J.K. Gillam and A.F. Lewis, J. Appl. Polymer Sci., 7, 2293 and also J. Polymer Sci. C6, 125 (1964).

44. M.I. Pope, Polymer, 8, 49 (1967).

45. Gas Effluent Analysis, W. Lodding, (editor), Arnold (1967).

46. W.M. Ayres and E.M. Bens, Anal.Chem., 33, 568 (1961).

47. R.N. Rogers, S.K. Yasuda and J. Zinn, Anal. Chem., 32, 672 (1960)

48. Reference 45, Chapter 5.

49. C.L. Rosen and A.J. Melveger, J. Phys. Chem., 5, 1079 (1964).

50. H.L. Friedman, J. Macromol. Sci. (Chem), A1, 57 (1967).

51. G.P. Shulman, J. Polymer Sci., B3, 911 (1965) and G.P. Shulman and H.W. Lochte, J. Appl. Polymer Sci., 10, 619 (1966).

52. A. Barlow, R.S. Lehrle and J.C. Robb, Polymer 2, 27 (1961).

53. A. Barlow, R.S. Lehrle, J.C. Robb and D. Sunderland, Polymer, 8, 523, 537 (1967).

54. I.C. McNeill, J. Polymer Sci., 44, 2479 (1966).

55. I.C. McNeill, Thermal Analysis Conference, Boston, (1968).

56. C.S. Marvel and C.L. Levesque, J. Amer. Chem. Soc., 60, 280 (1938).

57. C.S. Marvel, E.H. Riddle and J.O. Corner, J. Amer. Chem. Soc., 64, 92 (1942).

58. J.N. Hay, Makromol Chem., 67, 31 (1963).

59. K. Matzuzaki and T.C. Lay, Makromol Chem., 110, 185 (1967).

60. F.T. Wall, J. Amer. Chem. Soc., 64, 269 (1942).

61. J.N. Hay, PhD. Thesis, Glasgow University, pages 95-96 (1960).

62. R. Mecke and F. Langenbucher, Infra-Red Spectra, Heyden, Reference Spectrum 953 (1965).

63. K. Bowden, E.A. Braude and E.R.H. Jones, J. Chem. Soc., 948 (1946).

64. W. Cooper and E. Catterall, Chem. and Ind., 1514 (1954).

65. J. McKenna, R.I.C. Lecture Series 1, (1966).

66. I.C. McNeill, private communication.

67. I.C. McNeill and M.A.J. Mohammed, unpublished.

68. W. Millrine, B. Sc. Thesis, Glasgow University, (1966).

69. A. Barlow, R.S. Lehrle and J.C. Robb, Makromol Chem., 54, 230 (1962), also reference 25.

70. G.J. Knight, J. Polymer Sci. B, 5, 855 (1967).

71. W.C. Geddes, Europe Polymer J., 3, 267 (1967).

72. Reference 1, page 578.

73. R.B. Fox, in "Progress in Polymer Science" 1, A.D. Jenkins (Ed.), Pergamon, London (1967).

74. A.R. Schultz, Cleavage Reactions - Radiation, in "Chemical Reactions of Polymers", E.M. Fettes (Ed.), Interscience, (1964) pages 651 - 656.

75. V. Haber, J. Appl. Polymer Sci., 10, 1185, (1966).

76. I.C. McNeill and D.L. Gardner, unpublished.

77. R. McGuchan, PhD Thesis, Glasgow University, page 119 (1966).

78. J.B. Gilbert, J.J. Kipling, B. McEnaney and J.N. Sherwood, Polymer, 3, 1 (1962).
J.J. Kipling and R.B. Wilson, Trans. Faraday Soc. 56, 557 (1960). See also reference 19.

79. E.J. Lawton and J.S. Balwit, J. Phys. Chem., 65, 815 (1961)
I. Ouchi, J. Polymer Sci., A3, 2685 (1965).
See also F.H. Winslow, W.O. Baker and W.A. Yager, J. Amer. Chem. Soc., 77, 4751 (1955).

80. Reference 73, page 76.

81. E. Arlman, J. Polymer Sci., 12, 543 (1954).

82. A.A. Berlin, Doklady Akad. Nauk SSSR 114, 1042 (1962).

83. N. Grassie, Trans. Faraday Soc., 49, 835 (1953); ibid, 48, 379 (1952).

84. G. Talamini, G. Cinque and G. Palma, Mater. Plast. Elast., 30, 317 (1964); Chem. Abs., 61, 12147 (e).

85. N.L. Zutty and F. Welch, J. Polymer Sci., A1, 2289 (1963).

86. F.R. Mayo, F.M. Lewis and C. Walling, J. Amer. Chem. Soc., 70, 1529 (1948).

87. D.H. Richards and D.A. Salter, Polymer, 8, 127 (1967).

88. Y. Mizutani, S. Matsuoka and K. Yamamoto, Bull. Chem. Soc. Japan, 38, 2045, (1965).
Y. Mizutani, K. Yamamoto and S. Matsuoka, ibid, 39, 1792 (1966)
Y. Mizutani, K. Yamamoto, S. Matsuoka and S. Hisano, ibid, 40, 1526 (1967).

89. C. Vasile, F. Sandru, I.A. Schneider and N. Asandei, Makromol Chem., 110, 20 (1967).

90. A Dobry and F. Boyer Kawenoki, J. Polymer Sci., 2, 90 (1947).

91. L.J. Hughes and G.E. Britt, J. Appl. Polymer Sci., 5, 337 (1961) could be L. Bohn, Kolloid Z. u. Z. Polymere 213, 55 (1966).

92. Fettes and Maclay, Polymer Preprints 8, 2 (1967).

93. R.J. Kern and R.J. Slocombe, J. Polymer Sci., 15, 183 (1955).

94. R.J. Kern, J. Polymer Sci., 21, 19 (1956). Also ref 90.

95. D.H. Grant and N. Grassie, Polymer, 1, 125 (1960).

96. W. Hahn and F. Grafmüller, Makromol Chem., 21, 121 (1956) and F.H. Owens, F.E. Zimmermann, J. Polymer Sci., 2711 (1963).

97. I.C. McNeill and D.L. Gardner, unpublished.

98. I.J.M. Davidson, B.Sc. Thesis, Glasgow University (1968).

99. G.G. Cameron and D.R. Kane, Makromol Chem. 109, 194 (1967).

100. G.G. Cameron and D.R. Kane, Makromol Chem. 113, 75 (1968).

101. R. McGuchan, PhD. Thesis, Glasgow University (1966).

102. G.M. Burnett, R.A. Haldon and J.N. Hay, Europ Polymer J., 3, 449 (1967).

103. C.D. Doyle, Chapter 4 of Thermal Analysis (Volume 1 of Techniques and Methods of Polymer Evaluation, Slade and Jenkins, eds., Arnold (1966)).

104. H.E. Kissinger, Analyt. Chem. 29, 1702 (1957).

105. G.G. Cameron and J.D. Fortune, Europ. Polymer J., 4, 333 (1968).

106. S.L. Madorsky, J. Polymer Sci., 9, 133 (1952).

107. H.H.G. Jellinek, J. Polymer Sci. 4, 13 (1949).

108. D.A. Anderson and E.S. Freeman, J. Polymer Sci. 54 (1961).

109. H.H.G. Jellinek and M.D. Luh, Makromol Chem., 115, 89 (1968).

110. H.L. Friedmann, to be published.
